Chlorine, Bromine, Iodine

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Chlorine

Cl₂

Commercially available liquid chlorine, which is obtained by electrolysis of alkali, is not sufficiently pure and must therefore be purified by method I.

On the other hand, a gas that is already largely free of such impurities as O₂ and chlorine oxides is produced by the reaction of hydrated manganese dioxide with pure hydrochloric acid. For this preparation, see method II below.

I. Chlorine from a steel cylinder is passed consecutively through two wash bottles or columns containing concentrated H₂SO₄, a tube or column containing CaO (to remove any HCl that might be present), a tube containing P₂O₅, and finally into a container placed in a Dry Ice-acetone bath, where it is condensed and liquefied. The liquefied Cl₂ is repeatedly vaporized and condensed while noncondensable gases (O₂) are continuously removed with a pump. Finally, the liquid Cl₂ is fractionated in high vacuum and passed into receivers cooled with liquid nitrogen. (For the apparatus see, for example, Part I, p. 66 ff.) Only the middle fraction is used for further work.

II. \[ \text{MnO}_x \cdot \text{xH}_2\text{O}* + 4 \text{HCl} = \text{MnCl}_x + (x + 2)\text{H}_2\text{O} + \text{Cl}_2 \]

\[ \sim 100 \quad 145.88 \quad 70.91 \]

* \( x \sim 0.8 \) for a product of about 86% purity.

Concentrated, air-free hydrochloric acid (d 1.16) is added dropwise to precipitated hydrated manganese dioxide (e.g., the 86% pure commercially obtainable material) in a flask equipped with a dropping funnel and a gas outlet tube. The gas formation may be regulated by moderate heating.

The chlorine thus formed is passed through water (to remove entrained HCl) and H₂SO₄ (carried out as in method I, that is,
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H₂SO₄, a tube containing CaO, a tube with P₂O₅) and liquefied in a receiver cooled with a Dry Ice-acetone bath. Subsequent purification is as in method I.

Other preparative methods:

III. Electrolysis of an NaCl solution saturated with HCl in the electrolytic cell described by Bodenstein and Pohl. The oxygen content of the Cl₂ produced in this manner is 0.01%.

Extremely pure Cl₂ can be produced in small quantities by the following methods:

IV. Heating AuCl₃ (prepared from finely divided Au and dry Cl₂) at 250°C in vacuum.

V. Sublimation-crystallization procedure carried out in high vacuum. (In this process, the purity of the Cl₂ product is checked by measuring the rate of formation of phosgene from CO and Cl₂. This reaction is retarded by the slightest impurities.)

Klemenc considers the most effective means of removing the last traces of O₂ from Cl₂ to be the bubbling of very pure H₂ through liquid Cl₂ at −78°C for 24 hours.

PROPERTIES:

Yellow-green, pungent gas. M.p. −101.0°C, b.p. −34.0°C. Heat of fusion 1531 cal./mole; heat of vaporization 4878 cal./mole. Triple point pressure 10.4 mm., crit. t. 143.5°C, crit. p. 76.1 atm. dₗ (liq.) (−34°C) 1.557. Solubility in water: 1 vol. of water dissolves 4.6 vol. of Cl₂ at 0°C, 2.15 vol. at 20°C, 1.22 vol. at 50°C, 0.39 vol. at 90°C.

Chlorine attacks rubber, cork, stopcock grease and Hg but can be stored in glass containers over concentrated H₂SO₄ or as a liquid in steel cylinders. The vigorous reaction of chlorine with many commonly used metals occurs only at elevated temperatures; the reaction with steel, for example, starts above 250°C [G. Heinemann, F. G. Garrison and P. A. Haber, Ind. Eng. Chem., Ind. Ed. 38, 497 (1946)].

REFERENCES:


III. M. Bodenstein. Z. Elektrochem. 22, 204 (1916).


Chlorine hydrate

\[ \text{Cl}_2 \cdot 6\text{H}_2\text{O} \]

\[ \text{Cl}_2 + 6\text{H}_2\text{O} \rightarrow \text{Cl}_2 \cdot 6\text{H}_2\text{O} \]

1. Chlorine is dissolved in water at 0°C, forming a thin slurry which is then filtered through a glass filter funnel surrounded by a jacket cooled with ice water. The crystals, which are thus largely freed from water, are sealed into a glass tube and heated to 30 to 40°C. Decomposition into liquid Cl\(_2\) (under its own pressure) and Cl\(_2\)-saturated water results. The sealed tube is allowed to cool from 40 to 0°C in a large water bath for two days. Thus, the mixture components recombine and form larger crystals.

II. Better-formed crystals can be prepared in the following way:

Chlorine hydrate, prepared as above, is placed in one arm of a thick-wall U tube and the tube is sealed off. The hydrate is decomposed by heating and the chlorine formed is condensed by immersing the other arm of the U tube in a refrigerant. Then the refrigerant is removed while the other side of the tube, which contains water saturated with Cl\(_2\), is immersed in a vessel full of cold water. After some time large, very glittering, pale-yellow crystals are formed in this arm.

PROPERTIES:

Yellow crystals. Decomposition temperature at 1 atm. 9.6°C; critical decomposition point 28.7°C, 6 atm.; dissociation pressure (at 0°C) 252 mm.; d. (calc.) 1.29. Cubic crystals, with the theoretical composition of Cl\(_2\) • 5\(\frac{3}{4}\) H\(_2\)O.

REFERENCES:

Schröder. Die Chemie der Gashydrate [Chemistry of Hydrates of Gases], Stuttgart, 1926.
Even the purest commercial bromine contains approximately 0.05% Cl as well as traces of I, and must therefore be purified for special uses.

I. In order to remove most of the still present chlorine, bromine may be stored with pulverized KBr for a considerable time and then distilled off in high vacuum into a receiver cooled with a Dry Ice-ether mixture.

II. Very pure bromine may be prepared, according to Hönigschmid and Baxter, in the following manner: A concentrated solution of CaBr₂ or KBr is placed in a round-bottom flask connected with ground joints to a bromine-containing dropping funnel and to an exit tube, bent at right angles. The tube passes through a condenser into a receptacle containing ice-cold, very pure water. [The very pure CaBr₂ starting material is prepared by dropwise addition of bromine (which has been subjected to the purification described above) to ammoniacal calcium hydroxide. The calcium hydroxide is prepared from the very purest, halogen-free lime.] Bromine is added from the funnel to the flask and is then distilled off from the solution. As the Br₂ distills off, more bromine is added below the surface of the CaBr₂ (or KBr) solution from the dropping funnel. The distilled bromine is reduced to KBr by dropwise addition to a hot solution of recrystallized, halogen-free potassium oxalate. The KBr solution is evaporated. During evaporation, small quantities of Br₂ are liberated frequently by addition of acidified KMnO₄ solution, which through evaporation also removes any I₂ that may be present. According to Baxter, small quantities of absolutely pure Br₂ from a previous run may be added to achieve the same result. In order to decompose traces of organic materials, the KBr that crystallizes out is fused in a Pt crucible. It can then be considered completely free from Cl and I.

Bromine is now liberated by treatment of the KBr with very pure K₂Cr₂O₇ and very pure H₂SO₄ (the latter is obtained by distillation over K₂Cr₂O₇, discarding the forerun). However, the reaction with K₂Cr₂O₇ is not complete, since only about 75% of the needed K₂Cr₂O₇ enters into the reaction. Thus, the remaining Br₂ must be distilled again from the KBr solution formed. The product Br₂ is washed with water to remove HBr, separated from the entrained H₂O, and then dried over very pure CaO and CaBr₂ or over P₂O₅. Finally, it is freed of these substances by distillation in vacuum.
PROPERTIES:

Formula weight 159.84. Reddish-brown, pungent liquid. M.p. -7.3°C, b.p. 58.8°C; d (0°C) 3.19. Solubility in water (20°C) 3.53 g. of Br₂ per 100 g. of H₂O.

REFERENCES:


**Bromine Hydrate**

Br₂ · 8 H₂O

| Br₂ | + | 8 H₂O | = | Br₂ · 8 H₂O |
| 159.8 | 144 | 303.8 |

A 4% (by weight) solution of Br₂ in water (saturated solution at 0°C) is cooled to 0°C. This causes a small quantity of bromine hydrate (about 4% of the Br₂-H₂O mixture) to separate out. Usually, however, the solution must be either seeded with some bromine hydrate or cooled for a short time to -5°C, after which the temperature is restored to 0°C. The precipitate is filtered on a glass filter funnel surrounded by a jacket containing ice water.

In order to form larger crystals, the product hydrate is sealed into a tube together with a large excess of 4% bromine water and kept for about four weeks on ice. The tube is warmed to 5-6°C once each day.

PROPERTIES:

Light-red crystals, which must be stored in a sealed tube at temperatures below 6.2°C. Critical decomposition point: 6.2°C, 93 mm.; dissociation pressure (0°C), 45 mm.; d (solid) (0°C) 1.49.

The composition is somewhat uncertain. Cubic crystals have the theoretical composition Br₂ · 7²/₃ H₂O.

REFERENCES:

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Iodine

I₂

Since even the purest commercial KI to be used for the preparation of specially purified iodine may still contain such impurities as Cl, Br, ICN, alkali sulfate, carbonate and sulfide, as well as traces of organic material, special purification is necessary.

I. Preparation of very pure iodine according to Höngschmid.

\[
2\text{KI} + \text{CuSO}_4 \cdot 5\text{H}_2\text{O} = \text{CuI} + \text{K}_2\text{SO}_4 + \frac{1}{2}\text{I}_2 + 5\text{H}_2\text{O}
\]

A supersaturated solution of C.P. purity KI is mixed with a solution of thrice recrystallized, completely halogen-free CuSO₄ · 5H₂O. The CuI formed is allowed to settle and the supernatant solution of I₂ in KI is decanted and distilled. The I₂ is steam-distilled. The water is decanted from the condensate and the I₂ is again distilled from the KI solution and finally from pure water. After filtering through a glass frit, the iodine is dried in a desiccator over concentrated H₂SO₄ and finally sublimed in a quartz tube in a stream of nitrogen.

II. If extreme purification is unnecessary, commercial iodine or iodine regenerated from wastes can, according to a method described by Plotnikow, be sublimed, first over KI and then over BaO. It is then stored in ground glass containers placed in a desiccator over P₂O₅.

PROPERTIES:

Formula weight 253.84. Gray-black flakes with a metallic sheen. M.p. 113.7°C, b.p. 184.4°C; d 4.93. Solubility (20°C) 0.29 g./100 ml. of H₂O.

REFERENCES:

O. Höngschmid and W. Striebel. Z. phys. Chem. (A) 156a (Bodenstein Anniversary Volume), 286 (1931).
RECOVERY OF IODINE FROM LABORATORY WASTE SOLUTIONS

In the Arndt method, the oxidation of iodide residues with elementary oxygen, using nitric oxides as carriers, proceeds in accordance with the following reactions:

1. \[ HI + HNO_2 = \frac{1}{2}I_2 + NO + H_2O \]
2. \[ NO + \frac{1}{2}O_2 = NO_2 \]
3. \[ 2HI + NO_2 = I_2 + NO + H_2O \]
4. \[ 2NO_2 + \frac{1}{2}O_2 + H_2O = 2HNO_3 \]

This procedure is feasible because reaction 4 proceeds slowly in relation to reactions 1-3 so that, as long as iodine is present, no significant loss of nitric oxides occurs.

A large flask is closed off with a rubber stopper. A gas inlet is inserted through the stopper, reaching almost to the bottom; this tube is attached to the inlet tube of an empty wash bottle by a fairly long piece of flexible tubing; the other tube of the wash bottle is attached to a gasometer filled with \( O_2 \) from a cylinder. The alkaline solution of iodine residues, after concentration by evaporation, is placed in the flask, which should be no more than half full. It is then acidified with concentrated \( H_2SO_4 \) and the free space of the flask—with the stopper left loose—is filled with oxygen. The gasometer stopcock is then closed and nitrite solution is added to the flask until the free space acquires an intense reddish-brown color. The stopper is then pushed firmly down and the gasometer cock opened. The oxygen begins to flow into the closed flask either immediately or after very slight rotation of the stopcock. The flask is shaken, at first gently and then vigorously and continuously. The rate of oxygen absorption is checked from time to time by interrupting the shaking to determine whether \( O_2 \) is still flowing rapidly in and whether the gaseous phase is still reddish-brown. Should this not be the case, due to the accumulation of inert gases (from the \( N_2 \) in the \( O_2 \) used or from reduction of a small quantity of the nitric oxide to \( N_2O \) or \( N_2 \)), the stopper is raised for a moment. If this does not restore the \( O_2 \) absorption and the formation of \( NO_2 \), the stopcock is closed, further nitrite solution is added, and the procedure is continued. If shaking is started or stopped too quickly, some liquid may be driven into the wash bottle due to a temporary rise in pressure. However, the \( O_2 \) stream which again starts to flow drives it back into the flask. Completion of the oxidation may be recognized by the cessation of \( O_2 \) absorption and by the fact that the gaseous phase becomes colorless. After the black, crystalline iodine has settled, the completeness of the iodine precipitation may be checked by adding a few drops of nitrite solution. The mother liquor (which contains only about 0.5 g. of iodine per liter) is decanted and the iodine
precipitate is placed in a round-bottom flask, where it may be combined with iodine prepared in other runs. The I$_2$ is then steam-distilled from this flask. No condenser is used; instead, the vapor mixture is passed through a large tube (10-15 mm, in diameter) directly into the center of a large two-liter Erlenmeyer flask which is closed with a paraffin-coated cork stopper and immersed in a bath with flowing water. A second hole in the cork stopper contains a vent tube about 0.5 m, long and 1 cm. in diameter. The I$_2$ separates on the walls as a compact mass. The substance may easily be detached from these surfaces by shaking and cooling. It is crushed with a glass rod and suction-dried while pressing the water out.

The filtered I$_2$ is given a preliminary and final drying over CaCl$_2$ or concentrated H$_2$SO$_4$ in an ungreased desiccator and then sublimed. The iodine is placed in a spoutless beaker, which is immersed in a hot water bath while a round-bottom flask, filled with cold water, is set on top of the beaker. The flask becomes covered with moisture and some iodine and is replaced with a second flask before the condensed water can drop back. This is repeated as long as moisture is evolved. The end of the water evolution can be recognized by the fact that dry I$_2$ sticks firmly to the water-cooled glass, whereas moist iodine may easily be washed off the glass with a stream from a wash bottle. The wet beaker is now carefully wiped and carefully heated on an asbestos wire gauze. The round-bottom flask is now cooled on the inside with flowing water. As soon as a 0.5-1 cm. crust of iodine forms, it is scraped off and put in a storage flask. The sublimation is then continued until all the I$_2$ in the beaker has sublimed.

The method described must be modified in some cases, e.g.:

If the iodine residues contain considerable quantities of Fe, the oxidation must be carried out with heating in order to decompose Fe-NO complexes. If Hg or Pb salts are present, the procedure described in Chemiker-Ztg. 47, 16 (1923) is used.


If iodine is to be recovered from organic iodine compounds, the organic portion is decomposed with a KClO$_3$-Cl$_2$ mixture [E. M. Marshall, J. Chem. Ed. 7, 1131 (1930)].

Another procedure, based on reaction with Cl$_2$, is described by C. de Witt, J. Chem. Ed. 14, 215 (1937).

In collecting the iodine residues the greatest care should be taken to avoid the presence of any volatile organic solvents in the container. If nonvolatile organic materials such as starches are absent, the steam distillation described above may be omitted.
Great care should be taken to avoid contaminating the iodine residues with ammonium salts. Violent explosions may be caused by the formation of nitrogen iodide.

REFERENCES:

F. Arndt, Ber. dtsch. chem. Ges. 52, 1131 (1919).
F. Arndt, Chem. Ztg. 47, 16 (1923).

Hydrogen Chloride

HCl

I. An easily controllable stream of hydrogen chloride gas may be readily obtained by allowing pure, concentrated hydrochloric acid to flow into concentrated H₂SO₄.

An essential constituent of the apparatus shown in Fig. 143 is the capillary tube. This must be completely filled with hydrochloric acid before the evolution is started, in order to assure the hydrostatic pressure necessary to cause the lighter hydrochloric acid to flow to the bottom of the vessel which contains the heavier H₂SO₄. Only by allowing the acid to flow in this way is the generation of the gas completely uniform and controllable.

A separatory funnel is filled with approximately 200 ml. of concentrated H₂SO₄, and concentrated hydrochloric acid (d, 1.18) is added from a dropping funnel at such a rate as to give the gas flow desired. When 200 ml. of concentrated hydrochloric acid (i.e., the same volume as the volume of H₂SO₄ used) has been added, gas evolution stops and the dilute sulfuric acid, which now contains very little HCl, is discharged and replaced by fresh H₂SO₄. (If more than an equal volume of hydrochloric acid is added, HCl continues to be formed for a while after the stopcock is closed; however, the yield is reduced.) The yield from 200 ml. of concentrated hydrochloric acid is 67.4 g. of HCl.

If a uniform stream of HCl is required for a longer period, the apparatus designed by Seidel (Fig. 144) is recommended. Concentrated hydrochloric acid and concentrated sulfuric acid are dropped continuously from tubes a and b into the reaction tube,
which is about 5 cm. in diameter and contains a 20- to 25-cm. layer \(\sigma\) of packing, such as silica or glass beads. The spent liquid mixture automatically drains off below. With an apparatus of these dimensions, up to three liters of HCl gas can be produced per minute.

In order to remove moisture that may be present, the product gas is led through a wash bottle containing concentrated \(\text{H}_2\text{SO}_4\) (\(\text{P}_2\text{O}_5\) must not be used because the gas forms volatile phosphorus compounds with it) and into a receiver chilled with liquid nitrogen. The receiver is then detached from the generator and the gas is fractionally distilled. Only the middle fraction is pure enough for use in further work. (For the apparatus see Part I, p. 66 ff.)

If an especially pure product is not required, the ground glass part of the separatory funnel in Fig. 143 may be replaced by a two-hole rubber stopper. The freezing and fractional distillation of the hydrogen chloride may be omitted in this case.

**PROPERTIES:**


Attacks rubber and stopcock grease; glass stopcocks should therefore be lubricated with concentrated \(\text{H}_2\text{SO}_4\). The gas can be stored over Hg or over \(\text{H}_2\text{SO}_4\).

II. According to Hönigschmid, very pure aqueous solutions of HCl can be obtained by diluting pure laboratory hydrochloric acid to 20% with water, boiling it with small amounts of \(\text{KMnO}_4\) to remove bromine and iodine, and then distilling it through a quartz condenser. If the purified hydrochloric acid prepared in this way is needed in more concentrated form, HCl gas is generated from this dilute solution with \(\text{H}_2\text{SO}_4\) according to the method given under I, and this product gas is then bubbled through purified 20% hydrochloric acid until the latter becomes saturated.
Hydrogen Bromide
HBr

The method chosen for producing hydrogen bromide depends upon whether it is to be anhydrous or in aqueous solution, as well as on the amount required and the requisite degree of purity of the product.

Methods I and II, which are suitable for the preparation of anhydrous HBr, may also be modified to give aqueous solutions, but the special procedures for obtaining aqueous solutions (V) cannot be modified to give anhydrous HBr. However, regardless of the manner in which they have been prepared, HBr solutions can be dehydrated with P2O5 via method III.

While method I (tetralin plus Br2) is very convenient, it should be realized that half of the Br2 input is lost by reaction with the tetralin. Therefore, method II (H2 + Br2) is preferred for preparing larger quantities of HBr.

How far the described procedures can be simplified if a highly purified product is not required will be indicated under the respective methods.

I. Preparation of anhydrous HBr from tetralin (tetrahydronaphthalene) and Br2:

\[ C_{10}H_{12} + 4Br_2 = C_{10}H_8Br_4 + 4HBr \]

Bromine is gradually added by drops to a mixture of tetralin and pure iron filings contained in a round-bottom flask equipped with a dropping funnel and a gas outlet tube. (Prior to use, the tetralin is dried over anhydrous Na2SO4 and distilled; b.p. of the tetralin is 207°C, vapor pressure at 15°C, 0.3 mm.; C. P. grade Br2 should be used.) Since initial cooling is necessary, the flask is placed in a water bath, which, as soon as the reaction becomes sluggish, is heated to 30 to 40°C. The gas formed in the reaction is passed
through a wash bottle filled with tetralin (also predried and distilled) in order to eliminate small quantities of Br₂, and through a trap cooled to −60°C in order to remove the last traces of moisture. It is then frozen in a second trap cooled with liquid nitrogen. After completion of the reaction, the receiver trap is separated from the gas generating apparatus by melting the connection.

A more effective method for removal of the last traces of water involves trapping at −70°C instead of −60°C, so that some liquid HBr can accumulate through which the remaining HBr gas will bubble.

The condensed HBr is purified by subliming part of the solid product and collecting the middle fraction in a receiver cooled with liquid nitrogen. The container is then sealed off. The pressures in the preparation and fractionation sections of the apparatus should be monitored by means of an attached manometer. (For suitable apparatus, see Part I, p. 66 ff.)

II. \[ \text{H}_2 + \text{Br}_2 = 2 \text{HBr} \]

The arrangement shown in Fig. 145 is used; hydrogen bubbles through wash bottle \(A\), serving as a flowmeter. It then accumulates in flask \(B\), to which Br₂ can be added in drops from dropping funnel \(C\). The connecting tube from \(A\) must reach to the bottom of \(B\). Between \(A\) and \(B\) a part of the \(H_2\) stream is diverted to \(C\) so that when the closed-off vessel \(C\) is depleted, pressure equilibrium will be maintained. The \(H_2\) stream carrying the Br₂ vapor then enters Pyrex tube \(D\) (40-50 cm. long, 2-4 cm. in diameter), filled with platinized asbestos or platinized silica gel held in place by glass wool plugs. This tube is heated in electric furnace \(E\). The tube is connected to tube \(F\), which contains red phosphorus dispersed on glass spheres or Raschig rings, and to a wash bottle \(G\),

![Fig. 145. Preparation of hydrogen bromide.](image-url)
which contains a few milliliters of water to remove entrained phosphorus compounds. The HBr-H₂ mixture finally passes through a drying tube filled with CaCl₂ (CaBr₂ is better, of course) and is frozen in trap J by cooling with liquid nitrogen.

**Procedure:** Before adding the Br₂ to B, the air in the apparatus is displaced by a stream of H₂. When this has been accomplished, the furnace is heated to 350°C and the first portion of about 50 ml of Br₂ is admitted to container B. The H₂ should pass through the bromine layer (25°C) in a rather fast stream in order to assure a constant excess of H₂. Deterioration of the catalyst may be recognized by the increased presence of free Br₂ in the part of the apparatus connected to tube D. Care should be exercised to avoid channeling of the gas through tube D due to shrinkage of the catalyst. If no such precautions are taken, the H₂-Br₂ mixture is likely to emerge unconverted from the reactor.

The HBr frozen out in J is purified by fractional distillation as indicated in method I.

As a safety measure it is desirable that container B not be exposed to direct light. It is best to paint B black (leaving some peepholes in order to be able to check the amount of Br₂ present). When needed, rubber stoppers (which then must be frequently changed) and rubber tubing over the glass-to-glass connections may be used. Ground glass or fused joints are better, however. Because of the necessary pressure in the system, the stoppers on the wash bottles should be correspondingly well secured.

**Other preparative method:**

III. Dehydration of concentrated HBr solutions with P₂O₅. A round-bottom flask is partly filled with very pure P₂O₅; HBr solution is then added in drops from a dropping funnel, with simultaneous cooling. Purification of the gas stream thus produced is carried out as described in method I (A. Klemenc).

**Properties:**

Formula weight 80.93. Colorless gas. M.p. —87°C, b.p. —67°C; d₂₀ (-68°C) 2.17. A saturated solution in H₂O at 0°C contains 68.85% and at 25°C, 66% HBr. The constant-boiling acid at 760 mm. and 126°C contains 47.8% HBr.

Completely dry HBr may be stored for some time over Hg. After a while, decomposition sets in, possibly promoted by light and stopcock grease.

IV. Aqueous solutions of HBr may be prepared using the HBr prepared and purified according to I or II. If a less pure product is sufficient, it is possible to simplify the procedure in the following ways:

In method I: The HBr, after passing through the wash bottle containing tetralin, is led directly into water cooled with an
5. CHLORINE, BROMINE, IODINE

Ice-salt bath. The yield in this case is 94% of theoretical. When it is remembered that half the bromine is lost by combining with the tetralin, the yield based on total bromine reacted is 47%.

An even simpler method is to mix equal quantities of tetralin and water and then slowly drop Br₂ in with continuous stirring. The aqueous and nonaqueous layers are separated in a separatory funnel, the nonaqueous layer is again washed with H₂O, and the wash water is combined with the main HBr solution.

In method II: Drying tube H and trap J are replaced by one or more interconnected wash bottles containing water and cooled by an ice-salt bath. In this case, approximately 65% HBr solutions are obtained.

V.

\[
\text{H}_2\text{SO}_4 + \text{KBr} = \text{KHSO}_4 + \text{HBr}
\]

A direct method, which is suitable only for the preparation of constant-boiling HBr solutions, depends on the effect of dilute sulfuric acid on KBr (concentrated H₂SO₄ would oxidize the HBr to Br₂).

A mixture of 120 g. of pulverized KBr and 200 ml. of H₂O is chilled with cold water and slowly reacted with 90 ml. of concentrated H₂SO₄. The temperature should not be allowed to rise above 75°C to retard possible formation of free bromine. The solution is then cooled to room temperature and the KHSO₄ is filtered off through a Büchner funnel (using hard filter paper). The filtrate is placed in a 500-ml. distillation flask equipped with a suitable condenser and receiver and heated over a wire gauze. After distilling off the water, the fraction that is collected begins to boil 1° below the boiling point of the azeotrope [b.p. 122.5°C (740 mm.), 126°C (760 mm.)] and the distillation is stopped as soon as the temperature begins to drop. The yield is about 85%.

This acid may still contain about 0.01% H₂SO₄. Acid that is completely free of H₂SO₄—in the highest attainable concentration—is obtained if collection of the distillate is begun 5° below the boiling point of the constant-boiling acid. This distillate is then redistilled, but only the fraction at the boiling point of the azeotrope is collected.

REFERENCES:

I. A. Müller. Mh. Chem. 49, 29 (1928).

The choice of preparative method depends on whether anhydrous HI or an HI solution is required. Method I (preparation of anhydrous HI from \( \text{H}_2 \) and \( \text{I}_2 \)) is quite suitable for the preparation of HI solutions, while method III (\( \text{H}_2\text{S} + \text{I}_2 \)) is limited to solutions, unless (in accordance with II) the highly concentrated aqueous solution is dehydrated with \( \text{P}_2\text{O}_5 \). Since HI solutions soon turn brown on standing (due to the formation of iodine by light and air), a method (IV) for regenerating such solutions is also given.

\( \text{H}_2 + \text{I}_2 = 2\text{HI} \)

Hydrogen is passed over \( \text{I}_2 \) contained in a 250-ml. Pyrex flask \( \mathcal{A} \) (see Fig. 146) which can be heated. A Pyrex tube \( \mathcal{B} \), 90 cm. long and 1.8-2 cm. in diameter, is connected to the flask. If possible, this tube is fused on directly. If absolutely necessary it may be connected by a ground joint. However, in this case the joint is sealed on the outside with asbestos-waterglass mixture. The part of the tube nearest flask \( \mathcal{A} \) is filled for a length of 10-20 cm. with platinized asbestos or a mixture of asbestos with Pt sponge which is then heated to \( 500^\circ \text{C} \) in a furnace. The tube is followed by a U tube \( \mathcal{C} \) containing \( \text{CaI}_2 \) to dry the HI, a U tube \( \mathcal{D} \) with KI to remove the last traces of iodine, and a freezing trap \( \mathcal{E} \) which is cooled to \( -78^\circ \text{C} \). A \( \text{P}_2\text{O}_5 \) tube \( \mathcal{F} \) serves as protection against atmospheric moisture. It is advisable to provide a bypass tube for \( \text{H}_2 \). The bypass hydrogen stream may then be used as a carrier gas to carry unreacted iodine, or iodine formed by decomposition of HI, from the empty part of tube \( \mathcal{B} \) back to flask \( \mathcal{A} \). In order to do this, stopcock \( \mathcal{H}_1 \) is opened, and the two-way stopcock is turned to a position \( 180^\circ \) from that shown in Fig. 146. After cooling the catalyst, the \( \text{I}_2 \) is heated with a Bunsen burner and sublimed in a stream of hydrogen, which carries it into \( \mathcal{A} \).

Preliminary treatment of starting materials: Cylinder \( \text{H}_2 \) is, as usual, passed over a Pt catalyst and through a system of drying tubes. The purest available \( \text{I}_2 \) is used; it is dried in a vacuum over \( \text{P}_2\text{O}_5 \) and, in order to remove any remaining Cl and Br, is intimately mixed with 5% by weight of KI. For the platinized
asbestos, see the section on Platinum Metals; about 3 g. of asbestos fibers is saturated with 7 ml. of 10% H$_2$PtCl$_6$ solution; the damp mixture is evaporated to dryness with continuous stirring and the product is then heated to red heat.

**Procedure:** After $A$ has been charged with I$_2$, the air in the apparatus is carefully displaced by N$_2$, following which H$_2$ is passed through. (If H$_2$ were to be admitted while the apparatus still contained oxygen, the catalyst could promote an explosive reaction of the hydrogen-oxygen mixture.) The catalyst is now heated. The I$_2$ in flask $A$ is heated just enough to produce very small quantities of I$_2$ vapor in the part of tube $B$ that extends beyond the catalyst. Experience shows that the correct temperature of the I$_2$ is reached when the condensation zone in the iodine flask lies somewhat higher than the side arm. Some I$_2$ also condenses in the connecting tube between $A$ and the catalyst and must therefore be carefully sublimed from time to time with a Bunsen burner. (In general, care should be taken during the entire run to assure that there are no solid I$_2$ plugs at any point of the apparatus.) The HI product, after passing through purification tubes $C$ and $D$ (which may be omitted if a high purity product is not required), is frozen in $E$ and then repeatedly fractionated. At the end of the run, the catalyst is cooled in a stream of H$_2$.

II. Another preparative method for anhydrous HI consists in dehydration of highly concentrated HI solutions by P$_2$O$_5$. A round-bottom flask is partially filled with very pure P$_2$O$_5$. The HI solution is then added in drops from a dropping funnel, while the flask is cooled. The gaseous product is dried in an adjoining tube with P$_2$O$_5$. Further purification of the HI product proceeds in accordance with method I.

**Properties:**

Formula weight 127.93. Colorless gas. M.p. −50.9°C, b.p. −35.4°C; d, (0°C) 5.66. Solid or liquid HI can be stored at a low temperature away from light. Solubility at 0°C, 900 g. of HI/100 g. of H$_2$O.

![Fig. 146. Preparation of hydrogen iodide.](image)
No rubber tubing or stoppers should be used with HI, if at all possible. If greased stopcocks must be used, white vaseline is the most suitable lubricant.

III. Solutions of HI may be obtained if the product prepared according to I, instead of being condensed, is dissolved in water cooled in an ice-salt bath.

The following method may be used to prepare azeotropic aqueous HI solution:

\[ \text{H}_2\text{S} + \text{I}_2 = 2\text{HI} + \text{S} \]

A suspension of 120 g. of I\(_2\) in 150 ml. of H\(_2\)O is vigorously stirred in a wide-neck 500-ml. vessel with a three-hole stopper (for a gas inlet tube which reaches below the surface of the liquid, a gas outlet tube, and a stirrer). The stirrer must fit the walls of the vessel as closely as possible. A stream of H\(_2\)S is then absorbed by the suspension, the flow rate being controlled so as not to exceed the absorption rate. Any slight excess of H\(_2\)S leaves the reaction vessel through the gas outlet tube and goes either to a hood or is passed over the surface of a sodium hydroxide solution in a special flask; the outlet tube should not dip into the sodium hydroxide. After about an hour, the solution in the absorption flask becomes practically colorless due to the separation of considerable quantities of sulfur. The solution is then separated from the coarser sulfur particles by decantation and filtered through a glass frit to remove the fine sulfur. The H\(_2\)S, still dissolved in the solution, is removed by a short period of boiling, after which a test of the solution should not give a reaction for sulfide.

The solution is distilled from a 250-ml. distillation flask, using boiling chips to avoid bumping. The fraction boiling from 125 to 127°C is collected. The yield is about 90% based on the I\(_2\) used. The azeotropic acid (57% HI) boils at 126°C (760 mm.), d 1.70. It fumes strongly in air. Aqueous HI solutions must be stored in dark, well-sealed flasks. It is advisable to seal the storage flasks with paraffin. As a further precaution against oxidation, the air above the surface of the liquid may be displaced by an inert gas before sealing the flask.

IV. Concentrated HI solutions that have become brown due to the separation of iodine may be regenerated as follows:

\[ \text{I}_2 + \text{H}_3\text{PO}_4 + \text{H}_2\text{O} = \text{H}_3\text{PO}_3 + 2\text{HI} \]

The reaction is carried out in a 500-ml. ground glass flask which is equipped with an inlet tube for inert gas (N\(_2\), H\(_2\) or CO\(_2\)) and a fractionating column. The latter carries a dropping funnel.
(connected with a ground glass joint) on top. The iodine-containing HI solution is brought to near boiling with inert gas slowly passing through the flask. The hot solution is then reacted with 50% $\text{H}_3\text{PO}_2$ solution, added by drops until decolorization occurs (only a few milliliters are needed for this, depending on the iodine content). The dropping funnel is now replaced by a ground joint thermometer, and the azeotropic acid is distilled off at 125-127°C (760 mm.).

REFERENCES:

I and III. M. Bodenstein. Z. phys. Chem. 13, 59 (1894).

**Ammonium Iodide**

**NH$_4$I**

I. 

\[
\text{I}_2 + 2\text{NH}_3 + \text{H}_2\text{O}_2 = 2\text{NH}_4\text{I} + \text{O}_2
\]

253.8 34 34 289.8 32

Powdered iodine (100 g.) is reacted with 280 ml. of 10% ammonia water (i.e., double the stoichiometric quantity) and 600 ml. of 3% $\text{H}_2\text{O}_2$ (i.e., 33% excess). The $\text{I}_2$ dissolves and $\text{O}_2$ is evolved. In some cases, further $\text{H}_2\text{O}_2$ solution must be added until the reaction mixture becomes pure yellow. The solution is evaporated on a steam bath.

The colorless crystals that separate deliquesce rapidly in moist air.

II. 

\[
\text{NH}_8 + \text{HI} = \text{NH}_4\text{I}
\]

17 127.9 144.9

\[
(\text{NH}_4)_2\text{CO}_3 \cdot \text{H}_2\text{O} + 2\text{HI} = 2\text{NH}_4\text{I} + 2\text{H}_2\text{O} + \text{CO}_4
\]

114.1 255.8 289.9 36 44
A solution of HI and a solution of NH$_3$ or (NH$_4$)$_2$CO$_3$ are combined in stoichiometric quantities and evaporated until crystallization of NH$_4$I occurs.

To prepare completely iodine-free, colorless crystals (in a hydrogen atmosphere), see P. Wulff and H. K. Cameron, Z. phys. Chem. (B) 10, 350 (1930).

**Properties:**

Formula weight 144.96. Colorless, very deliquescent crystals. d. 2.56. Sublimes on heating. Solubility (25°C): 177 g./100 g. H$_2$O.

**References:**

I. T. C. N. Broeksmit. Pharm. Weekbl. 54, 1373 (1917).

**Potassium Iodide**

KI

In order to prepare very pure KI, C.P. HI solution is allowed to react with KHCO$_3$, and the KI formed is heated in a stream of H$_2$ to 725°C (m.p. 680°C).

**References:**


**Iodine Monochloride**

ICl

I$_2$ + Cl$_2$ = 2ICl

253.8 70.9 324.7

About 300 ml. of cylinder Cl$_2$ is condensed in a weighed 500-ml. flask surrounded by a Dry Ice-ether bath. Penetration of moisture into the flask must be avoided. Approximately half the stoichiometric quantity of I$_2$ is added to the chlorine in the flask. The
amount necessary is determined from the roughly estimated volume of Cl₂ but should be weighed exactly before being added (300 ml. = 468 g. of Cl₂ requires 1674 g. of I₂; half = 837 g. of I₂). The reaction mixture solidifies after addition of the I₂. The cold bath is removed, the flask is allowed to warm to room temperature, and the unreacted chlorine is thus removed by evaporation.

The flask and its contents are then weighed and, after subtracting the known weight of the empty flask and of the iodine added, the weight of Cl₂ reacted is obtained. This quantity is always larger than that corresponding to the formation of ICl with a given quantity of I₂, indicating that some ICl₃ has formed. Therefore, iodine equivalent to the excess Cl₂ is added.

The flask is closed with a glass stopper and allowed to stand 24 hours or longer at room temperature. The crude product (at least 1070 g.) is recrystallized once or twice for complete purification; the liquid ICl is cooled until about 80% of the material solidifies. The liquid portion is then discarded.

PROPERTIES:

Formula weight 162.38. Reddish-brown liquid at ordinary temperatures; exists in two solid modifications: α-ICl, ruby-red needles (m.p. 27.1°C); β-ICl, brownish-red plates (m.p. 13.9°C), labile form.

The boiling point at atmospheric pressure cannot be determined exactly since ICl decomposes at the boiling point into I₂ and Cl₂; however, it lies in the vicinity of 100°C. d. (liq.) (29°C) 3.10.

Vigorously attacks cork, rubber and the skin, forming very painful patches (antidote: 20% hydrochloric acid).

Not hygroscopic; however, I₂O₅ is formed on the vessel walls as a result of hydrolysis by the moisture of the air.

REFERENCES:


Iodine Monobromide

IBr

\[ I + Br = IBr \]

126.9 79.9 206.8

A weighed quantity of finely powdered iodine is reacted in a cooled, round-bottom flask with the stoichiometric quantity of
dry bromine (added in portions). The mixture is then heated at 45°C in a nitrogen stream for a few hours. Further purification is achieved by allowing the melt to cool slowly (in the absence of moisture), and after the material has crystallized, most of the remaining liquid is decanted and discarded. The flask contents are remelted and the process repeated several times.

The product is best stored under dry N₂ in a sealed container. Rubber stoppers should be avoided under any circumstances. It is best to work with IBr in closed systems since it attacks the eyes and mucous membranes rather vigorously.

**PROPERTIES:**

Brownish-black crystals with an odor similar to bromine. M.p. 40-41°C, b.p. 119°C; d. (0°C) 4.116, (50°C) 3.73. The vapor is largely dissociated.

**REFERENCE:**

V. Gutmann. Mh. Chemie 82, 156 (1951).

**Iodine Trichloride**

ICl₃

\[
I_2 + 3Cl_2 = 2ICl_3
\]

253.8 212.8 466.6

I. Since passing Cl₂ over I₂ gives impure products and poor yields, the method of Thomas and Depuis is recommended. In this procedure, iodine is added to excess liquid Cl₂, and the excess Cl₂ is then evaporated.

A 200-ml quantity of Cl₂ (10% excess) is condensed in a flask cooled by a Dry Ice-acetone bath and protected from moisture. Finely powdered I₂ (338.3 g.) is gradually added, whereupon orange ICl₃ immediately precipitates. To complete the reaction, the mixture is allowed to stand in a cooling bath for a few hours. The excess chlorine is distilled at room temperature into a second cooled container (where it may be reacted with more I₂). The yield of ICl₃ is quantitative (622 g.).

II. According to E. Birk, Cl₂ gas is passed over I₂, which is cooled by a Dry Ice-acetone bath to −79°C, until yellow droplets of excess Cl₂ are visible. The reaction mixture is allowed to remain in the cooling bath for a few hours and the Cl₂ is then evaporated at room temperature. The yield is theoretical.
III. According to G. Mann, a layer of 500 g. of powdered iodine is spread over 250 g. of finely powdered KClO₃ contained in a 1500-ml. Erlenmeyer flask. Then 250 ml. of water is added. Finally, 950 ml. of concentrated hydrochloric acid is added in small portions over a period of 45 minutes. The temperature should remain below 40°C. The cold solution is filtered through fritted glass; the ICl₃ crystals are recrystallized from alcohol and dried over CaCl₂ in vacuum. The yield, based on the I₂ used, is 75%.

PROPERTIES:

Formula weight 233.3. Loose, orange powder or long, yellow needles with a penetrating, pungent odor. Very corrosive to the skin and leaves painful brown patches.

M.p. 101°C under the pressure of its own vapor (16 atm.). Very volatile even at room temperature and must therefore be stored in well-sealed flasks. Vapor pressure 1 atm. at 64°C. The vapor is almost completely dissociated to ICl and Cl₂; at 77°C, dissociation to ICl and Cl₂ is complete. d. (−40°C) 3.203.

Used as a chlorinating agent and as an oxidant (e.g., in sulfide analysis), in the form of a 25–35% solution of ICl₃ in concentrated hydrochloric acid.

REFERENCES:


Polyhalides

Numerous compounds of this sort are known. The selection given here—with the exception of KI₃ · H₂O and HICl₄ · 4H₂O—is so chosen that to each of the previously described interhalogen compounds there corresponds a polyhalide which yields that compound on decomposition.
Potassium Triiodide

\[ \text{KI}_3 \cdot \text{H}_2 \text{O} \]

\[ \text{KI} + \text{I}_2 + \text{H}_2 \text{O} = \text{KI}_3 \cdot \text{H}_2 \text{O} \]

The theoretical quantity of \( \text{I}_2 \) is added to a hot, saturated solution of \( \text{KI} \); after the iodine dissolves, the mixture is cooled to \( 0^\circ \text{C} \), whereupon \( \text{KI}_3 \cdot \text{H}_2 \text{O} \) crystallizes out.

PROPERTIES:

Dark brown, hygroscopic prisms which melt in a sealed tube at \( 38^\circ \text{C} \) and liberate iodine at \( 225^\circ \text{C} \), leaving \( \text{KI} \).

For a discussion of the fact that anhydrous \( \text{KI}_3 \) is unstable at room temperature while the monohydrate is stable, see the references given under II.

REFERENCES:


Cesium Dichlorobromide

\[ \text{CsBrCl}_2 \]

I. \[ \text{CsCl} + \frac{1}{2} \text{Br}_2 + \frac{1}{2} \text{Cl}_2 = \text{CsBrCl}_2 \]

A solution of 16.9 g. of \( \text{CsCl} \) in 85 ml. of water is prepared and treated with 8 g. \( \text{Br}_2 \). The solution is then slightly heated in order to hold in solution the \( \text{CsClBr}_2 \) that is formed. The solution is then saturated with \( \text{Cl}_2 \); glittering yellow crystals of \( \text{CsBrCl}_2 \) form. These are filtered, washed with some water, and recrystallized from a small amount of water. A better yield is obtained if the \( \text{CsCl} \) is dissolved in only 45 ml. of water. The bromine is then added, red crystals of \( \text{CsClBr}_2 \) precipitate, and \( \text{Cl}_2 \) is then introduced without producing any harmful effects.

II. \[ \text{CsBr} + \text{Cl}_2 = \text{CsBrCl}_2 \]

According to Ephraim, \( \text{CsBrCl}_2 \) may also be produced by introducing \( \text{Cl}_2 \) into \( \text{CsBr} \) solution until saturation.
Cremer and Duncan carried out the same reaction, but used dry CsBr at room temperature.

PROPERTIES:

Glittering yellow crystals which melt in a sealed tube at 205°C but which, when heated in the open at about 150°C, evolve bromine, leaving CsCl. (If the salt is not stored in well-sealed flasks, an appreciable amount of halogen is given off even at room temperature.)

REFERENCES:


**Potassium Dichloroiodide**

\[ \text{KICl}_2 \]

I. DRY PROCESS:

\[ \text{KIBr}_2 + \text{Cl}_2 = \text{KICl}_2 + \text{Br}_2 \]

\[
\begin{array}{cccc}
325.8 & 70.9 & 236.9 & 159.8 \\
\end{array}
\]

Dry Cl\(_2\) is allowed to react with dry KIBr\(_2\) at room temperature. After a few minutes KICl\(_2\) is formed and the Br\(_2\) produced is carried off in the Cl\(_2\) stream. (When the reaction is continued for a longer period, KICl\(_4\) is formed instead.)

It is also possible to prepare KICl\(_2\) in a dry process by grinding KICl\(_4\) with KIBr\(_2\):

\[ \text{KICl}_4 + \text{KIBr}_2 = 2 \text{KICl}_2 + \text{Br}_2 \]

\[
\begin{array}{cccc}
307.8 & 325.8 & 473.8 \\
\end{array}
\]

and driving off the Br\(_2\) formed as a byproduct.

II. AQUEOUS PROCESS:

\[ \text{KI} + \text{Cl}_2 = \text{KICl}_2 \]

\[
\begin{array}{cccc}
166 & 70.9 & 236.9 \\
\end{array}
\]

Chlorine is introduced into a very concentrated solution of KI until the initially precipitated I\(_2\) redissolves. In order to prevent
further chlorination to KICl₄, finely pulverized KI is added until the I₂ that separates is redissolved—with slight heating if necessary. Crystallization occurs on cooling.

**PROPERTIES:**

Long, orange crystals, very unstable in air. Begins to soften at 60°C in a sealed tube; liberates the labile halogen at 215°C.

**REFERENCES:**


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**Cesium Dichloroiodide**

CsICl₂

\[
\text{CsCl} + \frac{1}{2}\text{I}_2 + \frac{3}{2}\text{Cl}_2 = \text{CsICl}_2
\]

168.4 126.9 35.5 330.8

A solution of 16.8 g. of CsCl in 170 ml. of water is prepared and, after addition of 2.7 g. of I₂, is brought almost to boiling. Chlorine is introduced into the hot solution until the I₂ dissolves. An excess of Cl₂ should be avoided to prevent formation of CsICl₄. On cooling, CsICl₂ crystallizes out. It may be purified, if necessary, by recrystallization from a small amount of hot hydrochloric acid (1:1) and washing with a small amount of cold hydrochloric acid.

**PROPERTIES:**

Orange crystals which melt at 238°C in a sealed tube, evolving labile halogen at 290°C. More stable than KICl₂.

**REFERENCE:**

H. L. Wells. Z. anorg. allg. Chem. 1, 96 (1892).

---

**Potassium Dibromoiodide**

KIBr₂

\[
\text{KI} + \text{Br}_2 = \text{KIBr}_2
\]

166 159.8 325.8

Since KIBr₂ crystallized from aqueous solutions always contains water of crystallization, it must be prepared in a dry process.
A given quantity of finely pulverized and dried KI is mixed with an equal quantity (by weight) of Br\(_2\) and the mixture allowed to stand in a sealed flask for three days. When the reaction ends, the product is freed from excess Br\(_2\) by placing the unstoppered flask in a desiccator over I\(_2\) or NaOH.

**PROPERTIES:**

Shiny red crystals which melt at 58°C in a sealed tube, evolving labile halogen at 180°C.

**REFERENCES:**


**Cesium Dibromoiodide**  
CsIBr\(_2\)

I.  
\[ \text{CsI} + \text{Br}_2 = \text{CsIBr}_2 \]

259.8 159.8 419.6

Finely pulverized and dried CsI (26 g.) is mixed with about 17 g. of Br\(_2\) and allowed to stand in a closed flask for about three hours. The excess Br\(_2\) is removed by allowing the open flask to stand in a desiccator over I\(_2\) or NaOH.

II.  
\[ \text{CsBr} + \frac{1}{2} \text{I}_2 + \frac{1}{2} \text{Br}_2 = \text{CsIBr}_2 \]

212.8 126.9 79.9 419.6

A solution of 21.3 g. of CsBr in 213 ml. of water is prepared and treated with 12.7 g. of I\(_2\) and 8 g. of Br\(_2\). On cooling, CsIBr\(_2\) crystallizes out.

**PROPERTIES:**

Glistening red crystals, stable in air. Melt at 243 to 248°C in a sealed tube, evolving labile halogen at 320°C. More stable than KIBr\(_2\).

**REFERENCES:**

II. H. L. Wells. Z. anorg. allg. Chem. 1, 94 (1892).
Potassium Tetrachloroiodide

\[ \text{KICl}_4 \]

I. DRY PROCESS:

\[ \text{KIBr}_2 + 2 \text{Cl}_2 = \text{KICl}_4 + \text{Br}_2 \]

325.8 141.8 307.8 159.8

Dry KIBr\(_2\) (see p. 296) is placed in a flask equipped with a glass stopper carrying an inlet tube (almost touching the bottom of the flask) and a gas outlet tube. Dry Cl\(_2\) is passed through for some hours; this removes the byproduct Br\(_2\) as soon as formed. The yield of KICl\(_4\) is quantitative. Within a few minutes after the chlorine is introduced, KICl\(_2\) is formed. Reaction with further quantities of Cl\(_2\) to produce KICl\(_4\) requires several hours.


The formation of a pure product in solution is questionable because of the following equilibrium:

\[ \text{KICl}_4 + \text{Cl}_2 + 3 \text{H}_2\text{O} \rightleftharpoons \text{KIO}_3 + 6 \text{HCl} \]

so the compound is better prepared in a dry process.

The formation of iodate can be sharply suppressed by adding hydrochloric acid and avoiding an excess of chlorine.

II. SOLUTION PROCESS:

\[ \text{KI} + 2 \text{Cl}_2 = \text{KICl}_4 \]

166 141.8 307.8

Concentrated KI solution is acidified with hydrochloric acid and chlorine is introduced. The weight increase should be controlled so as to avoid an excess of chlorine. The yield is 70%.

For preparation of KICl\(_4\) from KCl solution, I\(_2\) and Cl\(_2\), see the references under III.

PROPERTIES:

Golden yellow needles; m.p. 116°C in a sealed tube; in air, evolve ICl\(_2\) even at room temperature.

REFERENCES:

Tetrachloroiodic Acid

\[ \text{HICl}_4 \cdot 4 \text{H}_2\text{O} \]

\[ \text{HCl} + \text{ICl}_3 + 4 \text{H}_2\text{O} = \text{HICl}_4 \cdot 4 \text{H}_2\text{O} \]

36.5 233.3 341.8

A solution of 20 g. of \( \text{ICl}_3 \) in the stoichiometric quantity (6.9 ml.) of concentrated hydrochloric acid (d 1.19) is prepared and cooled to 0°C, whereupon \( \text{HICl}_4 \cdot 4\text{H}_2\text{O} \) precipitates out.

Properties:

Orange-yellow, deliquescent plates which vigorously attack the skin, paper, etc. Not very stable; decomposed by solvents.

Reference:


Dichlorine Oxide

\[ \text{Cl}_2\text{O} \]

\[ 2 \text{HgO} + 2 \text{Cl}_2 = \text{Cl}_2\text{O} + \text{HgO} \cdot \text{HgCl}_2 \]

433.2 141.8 86.9 488.1

I. According to Bodenstein and Kistiakowsky, chlorine dried with concentrated \( \text{H}_2\text{SO}_4 \) is passed over \( \text{HgO} \) loosely packed in a U tube (300-350 mm. long, 12 mm. in diameter). Shallow layers of \( \text{HgO} \) should be alternated with small glass-wool plugs. In order to maintain a uniform temperature between 18 and 20°C, the U tube is placed vertically in a water bath. The product is passed through a \( \text{P}_2\text{O}_5 \) tube and is then frozen in a vessel cooled with liquid nitrogen.

To obtain the best possible yield, the dry chlorine is mixed with dry air in a ratio of 1:2 to 1:3. The air flow rate can be measured in a bubble counter and, if necessary, can be regulated by intermediate stopcocks. To avoid any pressure in the apparatus, the \( \text{Cl}_2 \)-air mixture is aspirated over the \( \text{HgO} \) at about 400-600 mm. The system is protected against moisture by a trap cooled with liquid nitrogen or by a drying tube. About 15 g. of crude \( \text{Cl}_2\text{O} \) is formed in 4-6 hours.
The \( \text{Cl}_2\text{O} \) is purified by distillation at atmospheric pressure. The first few milliliters are discarded. The remaining \( \text{Cl}_2\text{O} \) is of satisfactory purity except for the last few milliliters.

The \( \text{HgO} \) used in the reaction is prepared as follows: yellow \( \text{HgO} \) is precipitated from \( \text{Hg(NO}_3\text{)}_2 \) solution with sodium hydroxide. It is then suction-filtered, washed, dried and heated to \( 200-250^\circ\text{C} \).

The only suitable stopcock lubricants are Kel-F or Teflon greases.

According to Wallace and Goodeve, the \( \text{Cl}_2\text{O} \) formed as described above may be purified by passing the crude condensate first over \( \text{P}_2\text{O}_5 \) and then over precipitated but not heated \( \text{HgO} \) to remove any traces of unreacted \( \text{Cl}_2 \). It is then fractionated three times.

**II. Solutions of \( \text{Cl}_2\text{O} \) in inert solvents.** As an example, 3.55 g. of \( \text{Cl}_2 \) is dissolved in 100 ml. of carbon tetrachloride, 12 g. (i.e., somewhat more than the theoretical 10.82 g.) of carefully dried \( \text{HgO} \) is added, and the slurry shaken for 1.5 hours in the dark. Then the \( \text{HgO} \cdot \text{HgCl}_2 \) and the excess \( \text{HgO} \) are filtered off through a fritted glass filter. The solution must be kept in the dark and, if possible, refrigerated with Dry Ice.

**PROPERTIES:**

Yellowish-brown gas, with strong, unpleasant odor; deep brown liquid. M.p. \(-116^\circ\text{C}\), b.p. \(3.8^\circ\text{C}\).

Dissolves easily in water (forming HCIO). At \(0^\circ\text{C}\), 1 vol. \( \text{H}_2\text{O} \) dissolves more than 100 vol. \( \text{Cl}_2\text{O} \).

The material can only be stored as a liquid or as a solid below \(-80^\circ\text{C}\). Explodes on mixing with organic materials.

**REFERENCES:**


5. Chlorine, Bromine, Iodine

Chlorine Dioxide

\[ \text{ClO}_2 \]

I. \[ 3 \text{KClO}_3 + 3 \text{H}_2\text{SO}_4 = 2 \text{ClO}_2 + \text{HClO}_4 + \text{H}_2\text{O} + 3 \text{KH}_2\text{SO}_4 \]

A mixture of 20 g. of KClO\(_3\) and 60 g. of washed and calcined sand is prepared in a 200-ml. round-bottom flask equipped with a special dropping funnel and a gas outlet tube (Fig. 147). The mixture is cooled with ice, and ice-cold, concentrated H\(_2\)SO\(_4\) is slowly added by drops. The ClO\(_2\) product, somewhat contaminated with Cl\(_2\), is aspirated over P\(_2\)O\(_5\) and condensed by cooling with liquid nitrogen. It is purified by fractionation. Only the middle fraction is used.

The above method carries a danger of explosion, and ClO\(_2\) may be prepared more safely if it is diluted by simultaneously formed CO\(_2\) as in method II:

II. \[ 2 \text{KClO}_3 + 2 \text{H}_2\text{SO}_4 + \text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O} = 2 \text{ClO}_2 + 2 \text{CO}_2 + \]

\[ + 4\text{H}_2\text{O} + 2\text{KH}_2\text{SO}_4 \]

A mixture of 122 g. of KClO\(_3\) (about one mole), 100 g. of C.P. oxalic acid (H\(_2\)C\(_2\)O\(_4\)·2H\(_2\)O, 0.8 mole), and a chilled solution of 108 g. (57 ml., 1.1 moles) of concentrated H\(_2\)SO\(_4\) (d. 1.84) in 400 ml. of H\(_2\)O is prepared in a 1.5-liter ground joint flask. The mixture is slowly heated on a steam bath, and the smooth stream of ClO\(_2\) and CO\(_2\) is passed through a P\(_2\)O\(_5\) drying tube and into a receiver cooled to \(-78^\circ\text{C}\). When a sufficient quantity of liquid ClO\(_2\) has collected, a stopcock located between the P\(_2\)O\(_5\) tube and the receiver is closed. The receiver is then cooled to \(-110^\circ\text{C}\) and the remaining CO\(_2\) removed by suction. Final purification is by fractionation, retaining only the middle fraction.

III. Other preparative methods have been reported: from solid NaClO\(_2\) and Cl\(_2\) (Hutchinson and Derby) and from AgClO\(_3\) and Cl\(_2\) (King and Partington).
PROPERTIES:

Formula weight 67.46. Yellow gas, M.p. -59°C, b.p. 9.9°C. The liquid is reddish brown, the solid is yellowish red. At -80°C the vapor pressure is almost zero. d (gas) 3.09, d (liq.) ~1.5.

IV. Solutions of ClO₂ in H₂O may be prepared by passing the ClO₂-CO₂ mixture produced in method II through water cooled by an ice-salt mixture. The ClO₂ is twenty times more soluble than CO₂. One vol. of H₂O at 4°C dissolves 20 vol. of ClO₂ (5.7%).

V. \[2\text{NaClO}_2 \cdot 3\text{H}_2\text{O} + \text{Cl}_2 = 2\text{ClO}_2 + 2\text{NaCl} + 6\text{H}_2\text{O}\]

Aqueous solutions of ClO₂ may also be prepared by passing a Cl₂-air mixture (maximum 5% Cl₂) through two fritted glass wash bottles containing a 10% solution of sodium chlorite. Mixing of the two gases in the proper proportions is carried out by passing the Cl₂ and air separately through two wash bottles filled with H₂O, adjusting the ratio by bubble counting, and combining the streams. The ClO₂ formed in the chlorite solution is swept in a stream of air into two consecutive fritted glass wash bottles filled with water. These are cooled in an ice-salt mixture to aid the absorption. When the NaClO₂ solution in the first wash bottle changes suddenly from brown to a weak yellowish-green, it is exhausted and should be refilled. It is then used as the second wash bottle in the series.

General Precautions for Handling ClO₂. Gaseous or liquid ClO₂ often explodes for no obvious reason. Stopcock grease on stopcocks and ground glass joints should be avoided; concentrated H₂SO₄ or fluorocarbon grease should be used as lubricants. It is best to confine the dropping funnels to the type shown in Fig. 147. Direct exposure to daylight should be avoided in preparation and storage of ClO₂ because ClO₂ decomposes easily on illumination. It is best to work in a darkened hood and to paint the outside of the containers black.

Chlorine dioxide attacks Hg; the Hg surface may be protected by a layer of H₂SO₄ for a short time. Containers filled with solid or liquid ClO₂ which are to be sealed off should be well cooled previous to sealing so that no gaseous ClO₂ is present.

As a safety measure in case of breakage, coating the reaction vessels with an adherent plastic film is recommended.

The maximum safe partial pressure of ClO₂ is 36 mm. (see Reference, under III).

REFERENCES:

I. M. Bodenstein, P. Harteck and E. Padelt. Z. anorg. allg. Chem. 147, 233 (1925).
II. W. Bray. Z. phys. Chem. 54, 569 (1906).


Dichlorine Hexoxide

$\text{Cl}_2\text{O}_6$

Formation of $\text{Cl}_2\text{O}_6$ by illumination of $\text{ClO}_2$ and also by illumination of a mixture of $\text{Cl}_2$ and ozone has been proven by Bodenstein, Harteck and Padelt.

According to Schumacher and Stieger, $\text{ClO}_2$ and ozone react as follows:

$$2 \text{ClO}_2 + 2 \text{O}_3 = \text{Cl}_2\text{O}_6 + 2 \text{O}_2$$

Chlorine dioxide (see p. 301, method II), diluted with CO$_2$, is introduced into vessel $\alpha$ (Fig. 148), cooled to $-10^\circ$C. Simultaneously, a stream of ozone-oxygen mixture containing about 8% ozone is added as shown. The flow rate of the ClO$_2$-CO$_2$ mixture is 1-2 liters/hour; that of the O$_3$-O$_2$ mixture is 2-4 liters/hour. After a few minutes, brown oily drops begin to form on the walls of $\alpha$; this is a solution of ClO$_2$ in Cl$_2$O$_6$.

The stopcocks must be greased with fluorocarbon lubricant because of the corrosive effect of Cl$_2$O$_6$, unless one prefers to use the glass valves suggested by Bodenstein.

When a sufficient quantity of the material has accumulated in $\alpha$, the apparatus is sealed off at $s_1$, $s_2$ and $s_3$, and vessel $\alpha$ is evacuated through $\nu$, while being immersed first in finely crushed Dry Ice and then in an ice-water bath. About 2/3 of the liquid is allowed to boil off to assure that all the ClO$_2$ has been removed from the Cl$_2$O$_6$. If the Cl$_2$O$_6$ is to be used immediately in a reaction, it is distilled from $\alpha$ into a reaction vessel attached at $\nu$.

Fig. 148. Preparation of dichlorine hexoxide.
In the same way, but using break-seal valves, Goodeve and Richardson prepared Cl$_2$O$_5$ of an especially high degree of purity.

**PROPERTIES:**

Formula weight 166.9. Deep red liquid. M.p. 3.5°C, b.p. 203°C (calcd.); d (3°C) 2.02. Vapor pressure (0°C) 0.31 mm.

Gaseous Cl$_2$O$_5$ is largely dissociated to ClO$_3$; the latter, even at room temperature, dissociates to ClO$_2$ and O$_2$ or to Cl$_2$ and O$_2$. Liquid Cl$_2$O$_5$ is considerably more stable. It is the least explosive of all the chlorine oxides; however, it does explode on contact with organic materials.

**REFERENCES:**

M. Bodenstein, P. Harteck and E. Padelt. Z. anorg. allg. Chem. 147, 233 (1925).

**Dichlorine Heptoxide**

Cl$_7$O$_7$

\[
2 \text{HClO}_4 + \text{P}_2\text{O}_5 = \text{Cl}_7\text{O}_7 + 2 \text{HPO}_5
\]

I. Receiver a in the apparatus shown in Fig. 149, which contains about 30 g. of loose P$_2$O$_5$ dispersed between Raschig rings, is cooled with liquid nitrogen for about 15 minutes before 4-5 ml. of 70% HClO$_4$ is added in drops from the dropping funnel. The tube of the funnel is bent so that it terminates in the vicinity of the cold wall of the receiver. In this way the heat of reaction is rapidly carried away and explosions are avoided. After completion of the addition of acid, the temperature of a is raised to −70°C, and after ten minutes to −25°C; the reaction mixture is allowed to stand for two hours at this temperature. The viscous mass in a is finally allowed to stand at 0°C for a long time to complete the reaction.

After reevacuating, a is slowly heated on a water bath to 90°C. The fraction that distills below 40°C is discarded: beginning with a bath temperature of 40°C, colorless liquid droplets are obtained in the liquid-nitrogen-cooled receiver which is attached to drying tower b (filled with P$_2$O$_5$ dispersed between Raschig rings).
According to Goodeve and Powney, lower chlorine oxides may be decomposed by passing the product gas over CuO wire, freshly reduced to copper and placed in a copper tube. However, the formation of lower chlorine oxides can be avoided in advance, according to J. J. Manley [J. Chem. Soc. (London) 121, 331 (1922)], if before the reaction ozone is passed for 0.5 to 3 hours over the P$_2$O$_5$ to be used. The temperature should be 175–200°C; the treatment oxidizes the lower phosphorus oxides which are responsible for the formation of the lower chlorine oxides. Excess ozone is then displaced with O$_2$.

If the Cl$_2$O$_7$ product is not colorless, it is fractionated in vacuum.

II. According to Meyer and Kessler, Cl$_2$O$_7$ may be successfully prepared—although with a yield of only 10%—by mixing one part by weight of anhydrous HClO$_4$ (e.g., 20 to 30 g.) and 3 to 4 parts by weight of pure calcined kieselguhr with a mixture of one part by weight of P$_2$O$_5$ and one part by weight of kieselguhr. The reaction flask must be cooled. The Cl$_2$O$_7$ is distilled off at 80–90°C (2 mm.) and collected in a receiver cooled to −78°C. The relatively high temperature of 80–90°C is necessary because kieselguhr absorbs considerable quantities of Cl$_2$O$_7$. For further purification, a fractionating column may be attached.

III. A solution of Cl$_2$O$_7$ in CCl$_4$ is prepared as follows: 50 g. of P$_2$O$_5$ is suspended in 120 ml. of CCl$_4$ in a 500-ml. round-bottom flask. The flask contents must be continually stirred and cooled to 0°C. Then 8.2 g. of a 70% aqueous solution of HClO$_4$ is slowly added, drop by drop. Next, most of the CCl$_4$ is distilled off at 0°C, using an aspirator, and the mixture is then heated for a while to 70–75°C at atmospheric pressure. It is then distilled at 80°C, whereupon a mixture of CCl$_4$ and Cl$_2$O$_7$ goes over and is trapped in a receiver cooled to −20°C.

When this yellowish mixture is heated for a short time to 80°C, Cl$_2$ and lower chlorine oxides volatilize and a colorless, approximately 7–8% solution of Cl$_2$O$_7$ remains. If a more concentrated solution is required, P$_2$O$_5$ is added to this mixture and the entire operation is repeated. A 20–25% solution may be obtained by repeating the procedure several times.

**General Precautions for Handling Cl$_2$O$_7$.** Dichlorine heptoxide is more stable than the other chlorine oxides; it will, however, explode on impact or in contact with a flame. The greatest source
of danger in the preparation is not so much in handling the \( \text{Cl}_2\text{O}_7 \) product, but rather in the manipulation of the anhydrous \( \text{HClO}_4 \) used as a starting material. The use of rubber and organic materials must be avoided; stopcocks must be lubricated with \( \text{H}_2\text{SO}_4 \) or \( \text{H}_3\text{PO}_4 \), or still better, with fluorinated hydrocarbon grease.

The synthesis must be planned so that only about 2 ml. of \( \text{Cl}_2\text{O}_7 \) is produced at a time.

**PROPERTIES:**

Formula weight 182.91. Colorless, very volatile oil. M.p. \(-91.5^\circ\text{C}\), b.p. \(82^\circ\text{C}\); d (0°C) 1.86. Vapor pressure (0°C) 23.7 mm.

**REFERENCES:**


**Bromine Oxides**

**BROMINE DIOXIDE, \( \text{BrO}_2 \)**

I. The preparation is carried out by ozonizing bromine in Freon 11 (\( \text{CFC}_3 \)) at a low temperature. A solution of 1 g. of bromine in about 50 ml. of Freon 11 is prepared in a refrigerated container. This solution is saturated with ozone at \(-50^\circ\text{C}\) for about 30 minutes. The ozone dissolves in the Freon, giving a blue color. The ozone flow is then shut off and the solution is left for about 30 minutes in the refrigerant until a slight precipitate forms. A stream of ozone (precooled to \(-78^\circ\text{C}\) in a glass spiral) is then passed through the solution until the bromine has reacted completely (about 5-7 hours). Moisture is kept out by means of a \( \text{P}_2\text{O}_5 \) tube. The \( \text{BrO}_2 \) forms as a solid precipitate with the color of egg yolk. The ozone and Freon are distilled off in a high vacuum. The product is very pure.

II. According to Schwarz and Schmeisser, \( \text{BrO}_2 \) may be prepared from \( \text{Br}_2 \) vapor and \( \text{O}_2 \) in a glow discharge, using a discharge tube cooled by liquid nitrogen, which also serves as a gas trap (compare Part I, p. 91, Fig. 74).

**PROPERTIES:**

Solid with the color of egg yolk. No definite melting point; decomposes to \( \text{Br}_2 \) and \( \text{O}_2 \) at temperatures in the region of 0°C. May explode if heated too rapidly.
5. CHLORINE, BROMINE, IODINE

REFERENCES:


DIBROMINE MONoxide, Br\textsubscript{2}O

Slow heating of Br\textsubscript{2}O\textsubscript{2} (which is stable at low temperatures) in high vacuum from —40°C upward causes it to decompose to Br\textsubscript{2}, O\textsubscript{2}, a white, unidentified oxide, and Br\textsubscript{2}O, which can be frozen out as a brown substance.

By separating the byproducts at −55°C, the Br\textsubscript{2}O may be obtained in the pure state.

REFERENCE:


Diiodine Pentoxide

\( \ce{I_2O_5} \)

Diiodine pentoxide may be prepared by thermal dehydration of iodic acid.

\[
2 \ce{HIO_3} = \ce{I_2O_5} + \ce{H_2O}
\]

Finely powdered HIO\textsubscript{3} is heated in a stream of dry air for several hours at a temperature of 240–250°C in a glass tube which is placed in an aluminum block or an electric furnace in order to maintain the temperature as precisely as possible.

In order to obtain a colorless or, at most, a pale pink product, which corresponds as far as possible to the composition \( \ce{I_2O_5} \), the following precautions should be kept in mind:

According to Lamb, Bray and Geldard, the HIO\textsubscript{3} produced from I\textsubscript{2} and HClO\textsubscript{3} (see HIO\textsubscript{3}, method III) is more suitable for producing colorless \( \ce{I_2O_5} \) than the HIO\textsubscript{3} produced from I\textsubscript{2} and HNO\textsubscript{3} or from I\textsubscript{2}, \( \ce{H_2O_2} \) and HNO\textsubscript{3}.

Special attention should be given to the careful purification and drying of the air stream. According to Moles, \( \ce{H_2SO_4} \) should be avoided. The air should be purified by passage through alkaline \( \ce{KMnO_4} \) solution and over solid KOH, Na wire and \( \ce{P_2O_5} \).
Decomposition of iodic acid begins at 70°C in accordance with the equation $3\text{HIO}_3 = \text{HIO}_3 \cdot \text{I}_2\text{O}_5 + \text{H}_2\text{O}$. This reaction is favored if some $\text{HIO}_3 \cdot \text{I}_2\text{O}_5$ or $\text{I}_2\text{O}_5$ is added in advance. Otherwise, rapid heating will cause the $\text{HIO}_3$ to melt at 110°C, which results in transition to $\text{HIO}_3 \cdot \text{I}_2\text{O}_5$. At 200°C, $\text{HIO}_3 \cdot \text{I}_2\text{O}_5$ begins to evolve water and decomposes to $\text{I}_2\text{O}_5$. At 240-250°C this reaction proceeds rapidly and thoroughly. Keeping the above facts in mind, Baxter recommends that $\text{HIO}_3$ be first heated for an adequate time at 100°C (first dehydration stage) and then for one hour at 240°C (second dehydration stage).

The final product from the method of Lamb, Bray and Geldard still contains 0.2% moisture; Baxter's product, 0.002%.

**PROPERTIES:**

White, hygroscopic crystals. Decomposition to $\text{I}_2$ and $\text{O}_2$ begins at 275°C and is rapid at 350°C. $d$ (25°C) 4.8.

**PROPERTIES:**

E. Moles and A. Perez-Vitoria. Z. phys. Chem. (A) 156 a (Bodenstein, Anniversary Volume 583, (1931).


**Hypochlorous Acid**

$\text{HClO}$

1. 

$$2\left[\text{Cl}_2 \cdot 6\text{H}_2\text{O}\right] + \text{HgO} = 2\text{HClO} + \text{HgCl}_2 + 11\text{H}_2\text{O}$$

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<td>357.8</td>
<td>216.6</td>
<td>104.9</td>
<td>271.5</td>
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<td>198</td>
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Chlorine hydrate (e.g., 300 g.) is shaken in a wide-mouth bottle for 15 minutes with 3/4 of its weight (e.g., 225 g.) of $\text{HgO}$ (prepared from $\text{HgCl}_2$ by precipitation with $\text{NaOH}$ and dried at 300°C). The semifluid mass is then vacuum distilled; distilling off 1/3 of the mixture and collecting the distillate in a receiver cooled to $-20$°C yields a greenish-yellow, 25% solution of $\text{HClO}$. This solution may be stored for some time at low temperature; it decomposes immediately, however, at 0°C.
A solution of Cl₂O in CC₁₄, cooled to 0°C, is mixed with water (0°C) in a separating funnel (the stopcock of which must under no circumstances be coated with stopcock grease) and shaken vigorously for three minutes. The CC₁₄ layer is removed; the aqueous solution contains HClO which is free of Cl₂.

**Properties:**

Can be stored only in aqueous solution and is in equilibrium with the anhydride Cl₂O. The latter can be extracted from the solution, using CC₁₄, for example.

**References:**


### Sodium Hypochlorite

\[ \text{NaClO} \cdot 5\text{H}_2\text{O} \]

\[ 2\text{NaOH} + \text{Cl}_2 + 4\text{H}_2\text{O} = \text{NaClO} \cdot 5\text{H}_2\text{O} + \text{NaCl} \]

Chlorine is led through a glass tube, widened at the end like a funnel, into an ice-cold solution of 50 g. of NaOH in 50 ml. of H₂O contained in a brown, 350-ml., wide-neck flask. The mixture soon becomes a slurry and it must be repeatedly shaken in order to cause further Cl₂ to be absorbed. The progress of the reaction is periodically checked by determining the weight. After about three hours, the weight increase is 35 g.; this is about 80% of the quantity of chlorine (43.7 g.) needed for complete saturation. The reaction is now interrupted and the NaCl which has precipitated out is filtered off on a glass frit funnel cooled with an ice-salt bath. The filtrate must likewise be cooled with a freezing bath, since disproportionation to chloride and chlorate occurs on warming. The filtrate is then placed in a cold bath at −40°C, in which it solidifies completely within half an hour. After slowly raising the temperature to −5°C, the crystals of NaClO · 5H₂O are filtered through a fritted glass filter, externally cooled with an ice-salt bath.

**Properties:**

Colorless crystals, melting at 18°C in their own water of crystallization. This melt decomposes easily. By dehydration in
vacuum (over concentrated H₂SO₄) at the lowest possible temperature, largely anhydrous NaClO may be obtained; however, it tends to decompose explosively. Decomposed by the CO₂ of the air.

Solubility (0°C) 29.3 g. of NaClO · 5H₂O/100 g. H₂O.

REFERENCES:


**Sodium Hypobromite**

NaBrO · 5H₂O

\[
\begin{align*}
\text{Br}_2 + 2 \text{NaOH} + 4 \text{H}_2\text{O} &= \text{NaBrO} \cdot 5\text{H}_2\text{O} + \text{NaBr} \\
160 &+ 80 &+ 209 &+ 103
\end{align*}
\]

A 40% sodium hydroxide solution (438 g., 306 ml.) is stirred and cooled to −3°C in a wide-neck, round-bottom flask closed with a three-hole rubber stopper (for a stirrer, dropping funnel and thermometer). Bromine (314 g., 100 ml., 90% of the quantity theoretically needed for 175 g. of NaOH) is slowly added (1–2 drops per second) with constant stirring. The temperature of the reaction mixture is held between −8 and −3°C. Insufficient cooling results in the formation of NaBrO₃; cooling below −8°C should be avoided to prevent slow solidification of the flask contents.

During the addition of bromine, NaBr·2H₂O separates out. After completion of the addition of the bromine, the mixture is allowed to stand for one hour at −8°C; it is then filtered from the easily filterable NaBr·2H₂O (about 180 g.) through a glass frit filter, the filtrate being collected in a suction flask cooled to −5°C.

The orange filtrate, with a content of about 60 g. of NaBrO per 100 ml., is supersaturated with NaBrO·5H₂O. In order to induce crystallization, it must be seeded with some crystals prepared as follows: a few milliliters of NaBrO solution in a test tube are cooled to −50°C while the walls are scratched with a thermometer, whereupon the entire tube contents solidify. By briefly warming the test tube with the hand, the thermometer with the adhering crystal mass can be removed. A small part of these crystals is used to seed a few milliliters of NaBrO solution in a test tube at −5°C. The pure NaBrO·5H₂O which crystallizes out is now used to seed the remaining solution, maintained at −3°C. The abundant precipitate of NaBrO·5H₂O obtained is in the form of well-formed needles. The yield from 100 ml. of the filtrate is about 55 g. of crude moist material containing about 78% NaBrO·5H₂O, 14%
NaBr·2H₂O, and 3% NaBrO₃. The remainder is water. The crystal mass is separated on a glass frit and immediately recrystallized from 2% NaOH in order to obtain the maximum possible separation of NaBr and NaBrO₃. About 30 ml. of base (at 20°C) is used for each 100 g. of crude material. The solution is then filtered and the filtrate cooled with an ice-salt mixture. The crystals that are filtered off (when damp, about 18 g. from 100 g. of crude crystals) are dried for 1-2 hours on a precooled (0°C) porous clay plate placed in a desiccator (0°C) filled with silica gel.

**PROPERTIES:**

Formula weight (NaBrO) 118.91. Yellow crystals, readily soluble in H₂O. May be stored at −20°C in a closed weighing vessel for a few days with only slight loss of NaBrO; decomposition, with formation of NaBr and NaBrO₃, begins immediately at 0°C and is complete within two days.

Analysis after drying for one or two hours on clay at 0°C; about 92% NaBrO·5H₂O, 2% NaBr·2H₂O, 1% NaBrO₃, 5% moisture.

**REFERENCE:**


---

**Potassium Hypobromite**

KBrO·3H₂O

\[ \text{Br}_2 + 2 \text{KOH} + 2 \text{H}_2\text{O} = \text{KBrO} \cdot 3 \text{H}_2\text{O} + \text{KBr} \]

This may be prepared from concentrated potassium hydroxide solution and Br₂ in a manner similar to that previously described for NaBrO·5H₂O. One mixes 465 g. (300 ml.) of 53% potassium hydroxide solution (245 g. of KOH and 220 g. of H₂O) and 314 g. (100 ml.) of Br₂. This solution (about 250 ml.) is filtered from precipitated KBr (at this point the solution contains about 70 g. of KBrO per 100 ml.), and 125 g. of KOH and 157 g. (50 ml.) of Br₂ are added with stirring. The temperature is −5 to −10°C. The precipitated KBr is again filtered. The filtrate, which contains about 83 g. of KBrO per 100 ml., is cooled to −40°C and seeded with several crystals obtained by cooling a portion of the filtrate to −80°C. After a short time a substantial yield of long, yellow needles of KBrO·3H₂O is obtained. The precipitate is filtered off and dried on a precooled clay plate for about 20 hours in a desiccator at −20°C.

**REFERENCE:**

Sodium Chlorite
NaClO₂·3H₂O

One method of preparation, based on the reaction of ClO₃⁻ with alkalis in the presence of H₂O₂, is given below. Other methods use, for example, SO₂ or Mn(OH)₂ instead of H₂O₂, or start with ClO₃⁻ and metals or amalgams.

\[
2 \text{ClO}_3^- + \text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O} + \text{H}_2\text{O}_2 = \text{Ba(ClO}_3^-)_{2} + 10\text{H}_2\text{O} + \text{O}_2
\]

\[
\begin{array}{cccc}
135 & 315.5 & 34 & 272.3 \\
& & & 180 & 32 \\
\end{array}
\]

\[
\text{Ba(ClO}_3^-)_{2} + \text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} = 2\text{NaClO}_2 \cdot 3\text{H}_2\text{O} + \text{BaSO}_4 + 4\text{H}_2\text{O}
\]

\[
\begin{array}{cccc}
272.3 & 322.2 & 289 & 233.4 \\
& & & 72.1 \\
\end{array}
\]

Chlorine dioxide is synthesized from 24.5 g. of KClO₃, 20 g. of oxalic acid, 21.6 g. (11.8 ml.) of concentrated H₂SO₄ (d 1.84) and 80 ml. of water, according to method II given in the section Chlorine Dioxide, and is introduced into an Erlenmeyer flask containing 200 ml. of ice-cold H₂O. The yellow-orange ClO₂ solution is shaken until it is decolorized with an excess of solid Ba(OH)₂·8H₂O (i.e., with more than the theoretical quantity of 31.6 g., because of carbonate impurities present) and with 12 g. of 30% H₂O₂. The BaCO₃ precipitate is filtered off. The filtrate is boiled and treated with solid Na₂SO₄ until the excess barium ion precipitates as BaSO₄. The BaSO₄ is filtered and the solution evaporated on a steam bath until crystals of NaClO₂·3H₂O separate. The yield is about 15.6 g. (54%).

PROPERTIES:
Formula weight 144.51. White, flaky crystals; may be dehydrated over KOH in a desiccator. Anhydrous NaClO₂ explodes on impact.

REFERENCES:

Chloric Acid
HClO₃

\[
\text{Ba(ClO}_3^-)_{2} + \text{H}_2\text{SO}_4 = 2\text{HClO}_3 + \text{BaSO}_4
\]

\[
\begin{array}{cccc}
322.3 & 98.1 & 169 & 233.4 \\
\end{array}
\]

A solution of 322 g. of barium chlorate in 500 ml. of boiling water is prepared. A hot mixture of 98 g. of concentrated H₂SO₄
(53.3 ml., d 1.84) and 53.3 ml. of H₂O is then slowly added with stirring. Care should be taken to assure that a small excess of Ba(ClO₃)₂ rather than of H₂SO₄ exists at the end of the addition. The BaSO₄ precipitate is allowed to settle for at least one hour. Then 2/3 of the clear solution is poured off and the remainder filtered through a Büchner funnel. The filtrate is combined with the decanted solution, yielding about 660 ml. of a 22% solution of HClO₃ (d 1.11). Evaporation of the solution in a vacuum desiccator over concentrated H₂SO₄ produces concentrations up to 40%. (The 40% solution corresponds to the composition HClO₃·7H₂O; d 1.28.)

Alternate Method: This method uses cation-exchange resins to exchange metal ions (e.g., Na⁺) for H⁺.

According to Samuelson, this procedure is possible with ClO₃⁻ (e.g., in the form of NaClO₃) while in the case of ClO⁻, BrO₅⁻, IO₅⁻, for example, the acid is reduced by the resin. Preparation of an approximately 10% HClO₃ solution, which then can be concentrated, may be carried out in accordance with a method described by Klement.

PROPERTIES:

Formula weight 84.46. Forms colorless solutions which may be stored in glass-stoppered bottles. Pure solutions undergo slight decomposition at 95°C; impure solutions decompose at as low as 40°C.

REFERENCES:

O. Samuelson. IVA. 17, 5 (1946).

Ammonium Chlorate

NH₄ClO₃

I. 2KClO₃ + (NH₄)₂SO₄ = 2NH₄ClO₃ + K₂SO₄

245.1 132.1 203 174.2

The directions will be found below under Ba(ClO₃)₂·H₂O, since NH₄ClO₃ is an intermediate product in that preparation. If NH₄ClO₃ is to be isolated as such, the NH₄ClO₃ solution, freed of alcohol, is evaporated before the addition of Ba(OH)₂ for crystallization (as described in the other procedure). Since the substance
thus prepared may still contain $\text{SO}_4^{2-}$, it may be preferable to follow the entire procedure for $\text{Ba(ClO}_3\text{)}_2$ and then prepare the desired $\text{NH}_4\text{ClO}_3$ from the easily purified $\text{Ba(ClO}_3\text{)}_2$ in accordance with method III.

II. $$\text{HClO}_3 + \text{NH}_3 = \text{NH}_4\text{ClO}_3$$

$$84.5 \quad 17 \quad 101.5$$

$$2 \text{HClO}_3 + (\text{NH}_4)_2\text{CO}_3 \cdot \text{H}_2\text{O} = 2\text{NH}_4\text{ClO}_3 + \text{CO}_2 + 2\text{H}_2\text{O}$$

$$168.9 \quad 114.1 \quad 203 \quad 44 \quad 36$$

A chloric acid solution is reacted with the stoichiometric quantity of $\text{NH}_3$ or $(\text{NH}_4)_2\text{CO}_3 \cdot \text{H}_2\text{O}$ and the solution placed in a desiccator over $\text{H}_2\text{SO}_4$ to crystallize.

III. $$\text{Ba(ClO}_3\text{)}_2 + (\text{NH}_4)_2\text{SO}_4 = 2\text{NH}_4\text{ClO}_3 + \text{BaSO}_4$$

$$\cdot \text{H}_2\text{O} \quad 132.1 \quad 203 \quad 233.4$$

Concentrated solutions of the reagents are brought together in stoichiometric ratios; after filtering off the $\text{BaSO}_4$, the solution is evaporated.

**PROPERTIES:**

Formula weight 101.5. Small, needle-shaped crystals, which are unstable and therefore cannot be stored for any length of time. Caution should be exercised in handling $\text{NH}_4\text{ClO}_3$ since the substance occasionally explodes without apparent cause. It is definitely explosive at temperatures above 100°C. If the material is spread in a thin layer in the open, it may be manipulated without danger. It readily dissolves in water.

**REFERENCES:**

II. I. W. Retgers. Z. phys. Chem. 5, 448 (1890).

**Barium Chlorate**

$$\text{Ba(ClO}_3\text{)}_2 \cdot \text{H}_2\text{O}$$

$$2\text{KClO}_3 + (\text{NH}_4)_2\text{SO}_4 = 2\text{NH}_4\text{ClO}_3 + \text{K}_2\text{SO}_4$$

$$245.1 \quad 132.1 \quad 203 \quad 174.2$$

$$2\text{NH}_4\text{ClO}_3 + \text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O} = \text{Ba(ClO}_3\text{)}_2 \cdot \text{H}_2\text{O} + 2\text{NH}_3 + 9\text{H}_2\text{O}$$

$$203 \quad 315.3 \quad 322.3 \quad 34 \quad 162$$

A mixture of 122.6 g. of $\text{KClO}_3$, 70 g. of $(\text{NH}_4)_2\text{SO}_4$ and 350 ml. of hot water is evaporated in a porcelain dish with constant stirring.
until a thin slurry forms. After cooling, a fourfold quantity of 80% ethyl alcohol is added, resulting in the separation of insoluble K$_2$SO$_4$ from the NH$_4$ClO$_3$. The K$_2$SO$_4$ residue is filtered and washed several times with alcohol. The filtrate is freed of alcohol by distillation. The NH$_4$ClO$_3$ residue (caution: NH$_4$ClO$_3$ has a tendency to explode) is reacted in a porcelain dish on a steam bath with a sufficient quantity of hot concentrated Ba(OH)$_2$·8H$_2$O solution [at least 160 g. of Ba(OH)$_2$·8H$_2$O dissolved in about 160 ml. of hot water] so that the ammonia odor disappears completely and the solution finally gives a definite alkaline reaction. It is then evaporated to dryness. The residue is dissolved in a fivefold quantity of H$_2$O, and CO$_2$ is bubbled through the solution until the precipitation of BaCO$_3$ is completed. The BaCO$_3$ is filtered off and the solution evaporated to crystallization.

**PROPERTIES:**

Colorless, columnar prisms. M.p. (anhydrous salt) 414°C; d 3.18. Solubility (0°C): 27.4 g.; (100°C) 111.2 g./100 g. of H$_2$O.

**REFERENCE:**


**Bromic Acid**

HBrO$_3$

$$\text{Ba(BrO}_3\text{)}_2 + \text{H}_2\text{SO}_4 = 2 \text{HBrO}_3 + \text{BaSO}_4$$

98 257.8 233.4

411.2

Finely powdered Ba(BrO$_3$)$_2$·H$_2$O (100 g.) is mixed with a cold solution of 15 ml. (27.6 g., i.e., 10% excess) of concentrated H$_2$SO$_4$ (d 1.84) in 275 ml. of H$_2$O. The reaction flask is placed in an ice-salt bath during the addition. Following the addition, the flask is left for several hours in the bath and frequently shaken. The flask contents are then diluted by at least a factor of two; the exact amount of Ba(OH)$_2$·8H$_2$O solution necessary to remove the excess H$_2$SO$_4$ is added [7.75 g. of Ba(OH)$_2$·8H$_2$O is needed for this], which causes further BaSO$_4$ precipitation. The mixture is allowed to settle and the clear HBrO$_3$ solution is then decanted; the BaSO$_4$ is filtered off and the filtrate combined with the decanted solution. The acid may be concentrated to 50% by vacuum evaporation at as low a temperature as possible.
PROPERTIES:

Formula weight 128.92. Colorless solution.

REFERENCE:

O. Burchard. Z. phys. Chem. 2, 814 (1888).

**Barium Bromate**

\[ \text{Ba(BrO}_3\text{)}_2 \cdot \text{H}_2\text{O} \]

\[
2 \text{KBrO}_3 + \text{BaCl}_2 \cdot 2 \text{H}_2\text{O} = \text{Ba(BrO}_3\text{)}_2 \cdot \text{H}_2\text{O} + 2 \text{KCl} + \text{H}_2\text{O}
\]

A solution of 334 g. of KBrO\(_3\) in 700 ml. of boiling water is prepared; a hot solution of 244 g. of BaCl\(_2\) \cdot 2H\(_2\)O in 400 ml. of H\(_2\)O is added. The mixture is cooled and the supernatant liquid is decanted. The residue is washed several times with 100-ml. portions of cold water and then suction-filtered. The yield is almost quantitative. For further purification the product may be recrystallized once or several times from boiling H\(_2\)O.

PROPERTIES:

White crystals. M. p. 260\(^\circ\)C (dec.); d. 3.99. Solubility (10\(^\circ\)C): 0.44 g.; (100\(^\circ\)C) 5.39 g./100 g. of H\(_2\)O.

REFERENCE:


**Iodic Acid**

\[ \text{HIO}_3 \]

Iodic acid may be prepared by oxidation of I\(_2\) with HNO\(_3\) or with a mixture of HNO\(_3\) and H\(_2\)O\(_2\), but even with a clear reaction mixture a pure white product seldom results (I and II). Colorless HIO\(_3\) is formed from I\(_2\) and HClO\(_3\), which in turn is prepared from Ba(ClO\(_3\))\(_2\) and H\(_2\)SO\(_4\) (III). The procedure based on the reaction of Ba(IO\(_3\))\(_2\) [prepared from Ba(ClO\(_3\))\(_2\) and I\(_2\)] with H\(_2\)SO\(_4\) is unsatisfactory, since it does not give a H\(_2\)SO\(_4\)-free product.
I.  

Twice sublimed I$_2$ (100 g.), in an Erlenmeyer flask covered by a water-cooled round-bottom flask, is heated to 70-80°C with pure fuming nitric acid until the solution becomes light yellow. The mixture is then evaporated to dryness on a steam bath, treated several times with some H$_2$O$_2$, and again evaporated to dryness. The residue is dissolved in concentrated nitric acid on a steam bath and the clear, colorless solution rapidly cooled in an ice bath. The crystals are suction-filtered on fritted glass and dried for several days in a desiccator over solid KOH. Large crystals may be obtained if a seeded HIO$_3$ solution in 20% HNO$_3$ is allowed to evaporate at room temperature or over CaCl$_2$ in a vacuum desiccator. The crystals are then filtered and washed with the minimum amount of water.

II.  

Finely divided I$_2$ (50 g.), which is best prepared by oxidation of an iodide solution with Cl$_2$, H$_2$O$_2$ or some other oxidizing agent, is placed in a 750-ml. flask and heated on a water bath (70°C) with 50 ml. of concentrated nitric acid, 25 ml. of 30% H$_2$O$_2$ (H$_2$O$_2$ free from organic stabilizers should be used) and 50 ml. of H$_2$O. A water-cooled, round-bottom flask is used to cover the reaction vessel. After repeated shaking, the reaction suddenly begins and the color fades. The addition of H$_2$O$_2$ is continued until all the I$_2$ present has reacted. The solution is then evaporated to dryness; the residue is redissolved in a minimum of water and treated as indicated below.

If organic material is present in the H$_2$O$_2$, the residue after evaporation is dark. If this is the case, the residue is heated two hours at 140-150°C and then for a while at 170-180°C; after cooling, the HIO$_3$ is extracted with a very small quantity of hot water, and this solution is filtered and crystallized.

Because of the great solubility of HIO$_3$, large losses occur during crystallization; therefore, aqueous HIO$_3$ solutions may be mixed with an equal volume of concentrated nitric acid and evaporated to one third their volume. This usually results in separation of HIO$_3$ even from hot solutions.

III.  

Iodine (100 g.) is mixed with a volume of HClO$_3$ solution containing 68.55 g. (3% excess) of HClO$_3$. The reaction flask is
equipped with an air inlet tube and an outlet tube to carry the Cl\textsubscript{2} into an absorption solution (e.g., NaOH). The reaction mixture is heated and, after the reaction begins, air is slowly passed through. The reaction is completed in about 20 minutes. The solution is then cooled and filtered to remove impurities [e.g., small quantities of Ba(IO\textsubscript{4})\textsubscript{2} from traces of barium ion in the HClO\textsubscript{4}]. The filtrate is evaporated to dryness in a dish, using vigorous agitation. It may also be recrystallized as described in methods I or II.

**PROPERTIES:**

Formula weight 175.93. Colorless crystals. M.p. 110°C (conversion to HI\textsubscript{3}O\textsubscript{2}); d (0°C) 4.629. Water is partially eliminated even at 70°C, especially if even a trace of HIO\textsubscript{3}·I\textsubscript{2}O\textsubscript{5} is present. Above 220°C, complete dehydration to I\textsubscript{2}O\textsubscript{5} occurs.

Solubility (0°C): 286 g. HIO\textsubscript{3}/100 ml. H\textsubscript{2}O; (25°C): 141 g. HIO\textsubscript{3}/100 g. HN\textsubscript{2}O\textsubscript{3} [d (25°C) 1.4].

Very readily soluble in water, but is not hygroscopic. Since HIO\textsubscript{3} is light sensitive, it is best to carry out the reaction in complete darkness to obtain a colorless product.

**REFERENCES:**

I. E. Moles and A. Perez-Vitoria. Z. phys. Chem. (A) 156a (Bodenstein Anniversary Volume), 583 (1931).


**Perchloric Acid**

\[ \text{HClO}_4 \]

\[ \text{KClO}_4 + \text{H}_2\text{SO}_4 = \text{HClO}_4 + \text{KHSO}_4 \]

I. A fractionating flask equipped with a ground glass stopper is connected, either directly or through a ground glass joint, to a 75-cm.-long condenser, which is in turn connected to a receiver cooled to −40°C (or, if sufficient, only to −20°C). The latter is connected, through a tube filled with soda-lime, to an aspirator.
The fractionating flask is charged with 25 g. of KClO₄ and 100 g. of H₂SO₄ (d 1.84) and the contents slowly heated on a bath at a pressure of 10-20 mm. The flask should be immersed in the heating bath only to the liquid level so that the vapor space will not become overheated. The reaction begins at about 90°C; further heating is carried out at such a rate that a temperature of 160°C is reached in about one hour. The reaction mixture is allowed to remain for about two hours at this temperature. By this time all the KClO₄ has dissolved; the HClO₄ is then distilled. The crude, yellowish distillate is immediately redistilled at 35-40°C and 10-20 mm., on a steam bath. It is advisable to use a ground joint boiling capillary in the second distillation, but this is not necessary for the first. Small quantities of ClO₂, which color the acid yellow, may be quickly and completely removed by passing dry air through the solution. Dark-yellow acid cannot be decolorized either by the passage of air or by vacuum distillation. II. Anhydrous acid may be prepared from commercial 70% aqueous perchloric acid solution by mixing it with a fivefold quantity of H₂SO₄ (95.6%) and distilling at 90 to 160°C at 20-30 mm. If the pressure falls below this value, loss of HClO₄ by volatilization occurs. Use the apparatus described in I.

General Precautions for Handling Anhydrous HClO₄. All connections in the apparatus, if not fused with a torch, must be made with ground glass joints lubricated with H₃PO₄, H₂SO₄ or HClO₄. Rubber stoppers and rubber tubing must not be used. If solid HClO₄·H₂O should form in the receiver during distillation—perhaps because of too rapid heating—the distillation should be stopped immediately. If carefully cleaned glassware and pure starting materials are used, the preparation of HClO₄ is not at all dangerous. The free acid should not come in contact with wood, because this may result in an explosion. Explosions always occur when organic material comes into contact with the anhydrous acid. The skin must be thoroughly protected from the anhydrous acid (painful, lingering wounds!). The acid may be stored for a long time below 0°C without decomposition. Acid residues should never be disposed of by pouring into a waste bucket, but should be either discarded (in portions) in the open or diluted with a large amount of cold water. Caution is advisable even under these conditions!

PROPERTIES:

Water-clear, mobile liquid which fumes slightly in the air at room temperature. d₂₀° 1.764. M.p. -112°C, b.p. 130°C (760 mm., extrapolated: the acid decomposes at about 90°C), 14°C (15 mm.), 16°C (18 mm.), 17.3°C (20 mm.), 39°C (56 mm.).
REFERENCES:

K. van Emster. Z. anorg. allg. Chem. 52, 270 (1907).


Alkaline Earth Perchlorates

HYDROUS PERCHLORATE

The hydrous perchlorates $\text{Mg(ClO}_4\text{)}_2 \cdot 6\text{H}_2\text{O}$, $\text{Ca(ClO}_4\text{)}_2 \cdot 4\text{H}_2\text{O}$, $\text{Sr(ClO}_4\text{)}_2 \cdot 4\text{H}_2\text{O}$ and $\text{Ba(ClO}_4\text{)}_2 \cdot 3\text{H}_2\text{O}$ are prepared from the corresponding oxides, carbonates, chlorides or nitrates by dissolving these in slightly more than the theoretical quantity of 70% $\text{HClO}_4$ (in the case of oxides, a slight excess of the oxide is used and later filtered off) and concentrating the solution by evaporation. The crystals that separate out are centrifuged and dried in a desiccator.

ANHYDROUS PERCHLORATES

These are prepared by heating the hydrous perchlorates to 250°C in a vacuum drying oven, at pressures ranging from 1 to 10 mm.

Another method is based on the reaction of solid alkaline earth carbonates with solid $\text{NH}_4\text{ClO}_4$ (the reactants are ground together in a ball mill) at 250°C and at pressures ranging from 1 to 10 mm., according to the following equation:

$$\text{MC}_3 \text{O}_3 + 2\text{NH}_4\text{ClO}_4 = \text{M(ClO}_4\text{)}_2 + \text{H}_2\text{O} + \text{CO}_2 + 2\text{NH}_3$$

REFERENCES:


Nitrosyl Perchlorate

$$\text{NOClO}_4$$

$$\text{NO}_2 + \text{NO} + 2\text{HClO}_4 = 2\text{NOClO}_4 + \text{H}_2\text{O}$$

An approximately 30% aqueous solution of $\text{HClO}_4$ (100 ml.) is evaporated in a porcelain dish until dense white fumes are evolved.
The remaining liquid (a mixture of HClO₄ mono- and dihydrates) is poured into a round-bottom flask. A mixture of NO and NO₂ is then introduced (prepared by dropwise addition of 68% nitric acid to NaNO₂).

From 11 to 16 g. of colorless, thin platelets of NOClO₄·aq. form; these are filtered on a Büchner funnel. The yield can be raised almost to theoretical (53 g.) if the filtrate is evaporated and the NO-NO₂ mixture is reintroduced.

After filtration, the crystals are placed in a desiccator and dried for several hours on porous clay over P₂O₅. It is also a good idea to prefill the desiccator with NO-NO₂ mixture.

After drying the material in a vacuum over P₂O₅ for several days, the water is completely removed and anhydrous NOClO₄ is obtained.

**PROPERTIES:**

Formula weight (NOClO₄) 129.5. White crystals which decompose with water to form NO, NO₂, HNO₃ and HClO₄.

**REFERENCES:**


**Nitryl Perchlorate**

**NO₂ClO₄**

I. \[ \text{HNO}_3 + 2 \text{HClO}_4 = \text{H}_3\text{OClO}_4 + \text{NO}_2\text{ClO}_4 \]

According to Goddard, Hughes and Ingold, NO₂ClO₄ is prepared by reacting anhydrous HNO₃ with anhydrous HClO₄ in a high-vacuum apparatus. The simultaneously formed H₃OClO₄ is reconverted to HNO₃ and HClO₄ by the addition of N₂O₅. The reaction is carried out in a nitromethane solution, from which the NO₂ClO₄ is obtained by crystallization.

II. According to Gordon and Spinks, dry air (0°C) is passed through a Siemens ozonizer at a rate of 12 liters/hour. The products (ozone and nitrogen-containing gases) are mixed with a much slower stream of chlorine dioxide in an adjacent vessel. White crystals, with the composition NO₂ClO₄, are deposited on the walls of the reaction vessel.
Goddard, Hughes and Ingold call this compound nitronium perchlorate; Gordon and Spinks call it nitroxyl perchlorate.

PROPERTIES:

At 120°C, the compound decomposes rapidly, but not at an explosive rate.

For other information on the reaction between HNO₃ and HClO₄, see A. Hantzsch, Ber. dtsch. chem. Ges. 58, 958 (1925).

REFERENCES:


Periodic Acid

H₅IO₆

Since H₅IO₆ is decomposed catalytically by Pt, electrolysis on Pt cannot be used. The procedure described below, using barium periodate and HNO₃, makes use of the fact that Ba(NO₃)₂ is insoluble in concentrated HNO₃, while H₅IO₆ is soluble.

\[
\text{Ba}_3\text{H}_4(\text{IO}_6)_2 + 6 \text{HNO}_3 = 2 \text{H}_5\text{IO}_6 + 3 \text{Ba(NO}_3)_2
\]

A 100-g. quantity of Ba₃H₄(IO₆)₂ is moistened with 75 ml. of H₂O and treated with 200 ml. of colorless nitric acid (d 1.42). The agitated mixture is heated to 60-70°C for an hour and is then cooled to 30-40°C. The precipitated Ba(NO₃)₂ is filtered off on a glass frit. The residue is washed free of periodate by stirring with concentrated nitric acid. The combined filtrate is evaporated at 60-70°C in aspirator vacuum [if more Ba(NO₃)₂ separates, it is filtered and the evaporation continued] until H₅IO₆ begins to precipitate. After cooling, glistening crystals of periodic acid are formed. Since the solution tends to become supersaturated, it is often necessary to wait a long time. The crystals are filtered off and dried in a vacuum at 50°C. A second crystal crop may be obtained from the mother liquor by evaporation. The yield is almost quantitative (46 g. vs. the theoretical 52.9 g.).

No rubber tubes or rubber stoppers may be used in this procedure because they would reduce HNO₃ to lower oxides, which in turn would reduce H₅IO₆ to HIO₃.
5. CHLORINE, BROMINE, IODINE

PROPERTIES:

Formula weight 227.96. Colorless, hygroscopic crystals which decompose into \( \text{H}_2\text{O}, \text{O}_2 \) and \( \text{I}_2\text{O}_5 \) at the melting point (130°C).

REFERENCE:


Sodium Periodates

\( \text{Na}_3\text{H}_2\text{IO}_6, \text{NaIO}_4 \)

The syntheses of \( \text{Na}_3\text{H}_2\text{IO}_6 \) and \( \text{NaIO}_4 \) use \( \text{NaIO}_3 \) as the starting material. The latter is either used as such, or in the form of a solution which may easily be prepared from elemental iodine and excess \( \text{NaClO}_3 \) in the following manner.

A solution of 125 g. of pure \( \text{NaClO}_3 \) in 500 ml. of \( \text{H}_2\text{O} \) is prepared at 45°C in a five-liter flask. The solution is acidified with 2 ml. of concentrated nitric acid. Iodine (100 g.) is then added and an inverted beaker placed over the mouth of the flask to avoid loss of iodine. The reaction mixture is then heated, with constant agitation, to 50-70°C. If the reaction becomes too violent, the flask is cooled by immersion in cold water. The end of the reaction (in about 15 minutes) may be recognized by the disappearance of the iodine color. This solution may be used for the preparation of Na periodate. For each 100 g. of \( \text{I}_2 \), 76.9 g. of \( \text{NaClO}_3 \) is required, and 156.1 g. of \( \text{NaIO}_3 \) is produced.

\( \text{Na}_3\text{H}_2\text{IO}_6 \):

I. \( \text{NaIO}_3 + 4 \text{NaOH} + \text{Cl}_2 = \text{Na}_3\text{H}_2\text{IO}_6 + 2 \text{NaCl} + \text{H}_2\text{O} \)  
197.9  160  70.9  293.9  116.9  18

Solid \( \text{NaOH} \) (140 g.) and, if necessary, another 100 to 200 ml. of \( \text{H}_2\text{O} \) are added to a beaker containing the iodate solution prepared from 100 g. of \( \text{I}_2 \) as described above (alternately, 156.1 g. of \( \text{NaIO}_3 \) may be used). The mixture is vigorously boiled and \( \text{Cl}_2 \) is introduced as rapidly as possible through a glass tube at least 1 cm. in diameter. This also serves to agitate the reaction mixture continuously and vigorously. After about 10-15 minutes all the alkali is neutralized and no further \( \text{Cl}_2 \) is absorbed. The solution is then made slightly alkaline with \( \text{NaOH} \) in order to convert the small amount of the \( \text{Na}_2\text{H}_4\text{IO}_6 \) byproduct into the less soluble \( \text{Na}_3\text{H}_2\text{IO}_6 \). On cooling, the precipitate is filtered on a
M. SCHMEISSER

Büchner funnel. The precipitate is washed with cold water and dried at 110°C. The yield is about 225 g. (about 97% of the theoretical yield of 231.8 g.).

**Other preparative methods:**

II. If cylinder chlorine is unavailable, NaIO₃ may be oxidized with K₂S₂O₈ [the use of (NH₄)₂S₂O₈ is not recommended because of poor yields]. Using this method, some sulfate contamination of the product must be expected.

\[
\text{NaIO}_3 + \text{K}_2\text{S}_2\text{O}_8 + 4 \text{NaOH} = \text{Na}_3\text{H}_2\text{IO}_6 + \text{K}_2\text{SO}_4 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}
\]

The NaIO₃ solution prepared as above from 100 g. of I₂ (or a solution of 156.1 g. of NaIO₃) is gradually reacted with 40 g. of NaOH; it is then diluted with H₂O to a total volume of 1200 ml. and is then heated to boiling. The stoichiometric quantity (213 g.) of K₂S₂O₈ is then gradually added, followed by 170 g. of NaOH, added in portions. Continuous, vigorous stirring is necessary during the addition; a power agitator is preferable. Following the addition, the mixture is boiled for another 15 minutes, cooled to 40°C, and filtered through a fritted glass filter. A considerable amount of sulfate crystallizes on cooling below 40°C. The Na₃H₂IO₆ precipitate is washed several times with cold water.

III. The compound may also be prepared from NaI, Br₂ and NaOH:

\[
\text{NaI} + 4 \text{Br}_2 + 10 \text{NaOH} = \text{Na}_3\text{H}_2\text{IO}_6 + 8 \text{NaBr} + 4 \text{H}_2\text{O}
\]

A solution of 50 g. of NaI and 264 g. of NaOH in two liters of H₂O is prepared in a four-liter breaker. The solution is heated to 80°C and, while mechanically stirred, is gradually reacted with 80 ml. of Br₂ (2 ml./minute). The bromine is added from a dropping funnel with its tube projecting below the surface of the liquid. During the addition the temperature is kept as close as possible to 80°C. A precipitate suddenly forms after 30-45 minutes. The drop by drop addition of Br₂ is continued. By a quick movement of the flask, the liquid is decanted from the precipitate and the remainder of the Br₂ is added to the liquid, which is then recombined with the residue. The Na₃H₂IO₆ is now filtered through a fritted glass filter, washed four times with 25 ml. of H₂O and air dried. The yield is about 85 g. (87%).

NaIO₄:

\[
\text{Na}_3\text{H}_2\text{IO}_6 + 2 \text{HNO}_3 = \text{NaIO}_4 + 2 \text{NaNO}_3 + 2 \text{H}_2\text{O}
\]

A 100-g. quantity of Na₃H₂IO₆ is treated with 200 ml. of H₂O and 55 ml. of concentrated nitric acid (20% excess). If the liquid
is not clear, it is filtered through fritted glass. The filtrate is evaporated until crystals form. It is then cooled to 20°C (cooling to a lower temperature causes NaIO₄·3H₂O to crystallize out) and the precipitate is filtered off, washed with cold H₂O and dried at 110°C. The yield is about 61 g. (84%). The periodate still contained in the solution may be recovered as the rather insoluble KIO₄ (about 11 g.) by precipitation with KNO₃.

**PROPERTIES:**


**REFERENCES:**

E. Müller and W. Jakob. Z. anorg. allg. Chem. 82, 308 (1913).

**Potassium Periodate**

KIO₄

The preparation is analogous to that of sodium periodate: I₂ is converted to KIO₃ by means of KClO₃ and the KIO₃ is oxidized with Cl₂.

The KIO₃ solution obtained from 100 g. of I₂ and 135 g. of KClO₃ (or a solution of 168.6 g. of KIO₃) is treated with 195 g. of pure KOH (correspondingly more KOH if hydrous), and chlorine is passed through as previously described. The K₄I₂O₉ remains dissolved in this alkaline solution and KIO₄ may be precipitated by making the solution neutral or weakly acidic. The yield is almost quantitative (about 178 g.).

**PROPERTIES:**

White crystals. d 3.618. Solubility (13°C): 0.66 g. KIO₄/100 ml. H₂O.

**REFERENCES:**

Barium Periodate

\[ \text{Ba}_3\text{H}_4(\text{IO}_4)_2 \]

I. \[ 2\text{Na}_3\text{H}_2\text{IO}_6 + 3\text{Ba(NO}_3)_2 = \text{Ba}_3\text{H}_4(\text{IO}_4)_2 + 6\text{NaNO}_3 \]

The \( \text{Na}_3\text{H}_2\text{IO}_6 \) (about 225 g.) obtained from 100 g. of \( \text{I}_2 \), following the directions for \( \text{Na} \) periodate, is dissolved in one liter of \( \text{H}_2\text{O} \) and the solution, to which 10 ml. of concentrated nitric acid has been added, is heated to boiling. It is then treated with a hot aqueous solution of 425 g. of \( \text{Ba(NO}_3)_2 \). The mixture is boiled for 1.5 to 2 hours with vigorous stirring, then neutralized with \( \text{Ba(OH)}_2 \) and left to cool. The barium periodate that crystallizes out is repeatedly washed with hot water and the supernatant liquor decanted. It is finally filtered on a Büchner funnel. The yield is about 330 g.; however, the product still contains some \( \text{NaNO}_3 \).

II. By starting with \( \text{KI}_4 \), the product may be prepared according to the following equation:

\[ 2\text{KIO}_4 + 3\text{Ba(NO}_3)_2 + 4\text{KOH} = \text{Ba}_3\text{H}_4(\text{IO}_4)_2 + 6\text{KNO}_3 \]

The procedure is identical to that given above. However, if 100 g. of iodine or 181.2 g. of \( \text{KI}_4 \) is used as the starting material, another 88.4 g. of \( \text{KOH} \) should be added before the introduction of \( \text{Ba(NO}_3)_2 \).

PROPERTIES:

Formula weight 861.9. White crystals.

REFERENCE:


Chlorine Nitrate

\( \text{CINO}_3 \)

\[ \text{Cl}_2\text{O} + \text{N}_2\text{O}_5 = 2\text{CINO}_3 \]

86.9 108.0 194.9

A refrigerated pocket-shaped receiver is used to sublime an excess of \( \text{N}_2\text{O}_5 \) directly onto \( \text{Cl}_2\text{O} \) in high vacuum. The receiver
containing the Cl₂O (equivalent to 5 ml. of liquid) is placed in liquid nitrogen so that only the portion holding the Cl₂O is cooled, and the N₂O₅ thus deposits on the Cl₂O as a solid. After releasing the vacuum, the receiver is removed from the high-vacuum apparatus, closed off by means of a drying tube, and placed in a refrigerating bath at —78°C. While the bath is slowly warmed to between —20 and 0°C (over a period of 15 hours) the components react slowly with each other. The ClNO₃ thus formed is still contaminated with chlorine (an impurity of the Cl₂O) and excess N₂O₅.

In order to eliminate the chlorine, which is difficult to separate, the reaction product is heated to 30°C on a water bath and refluxed for one hour. The upper half of the reaction vessel (serving as a condenser) is cooled by a ring-shaped cup filled with Dry Ice. In this procedure the chlorine is volatilized, while the excess N₂O₅ is decomposed to NO₂ and O₂. The ClNO₃ is then distilled at —90°C in high vacuum, leaving behind the NO₂.

**PROPERTIES:**

**REFERENCES:**
M. Schmeisser. W. Fink and K. Brändle, Angew. Chem. 69, 780 (1957).

**Dipyridineiodine (I) Perchlorate**

\[ [I(C₅H₅N)₂]ClO₄ \]

This compound is prepared in pyridine solution as follows:

\[
\text{AgClO}_4 + 2 \text{C}_₅\text{H}_₅\text{N} = [\text{Ag(C}_₅\text{H}_₅\text{N)}₂]\text{ClO}_₄
\]

\[
[\text{Ag(C}_₅\text{H}_₅\text{N)}₂]\text{ClO}_₄ + I_₂ = \text{AgI} + [I(C₅H₅N)₂]\text{ClO}_₄
\]

**PROPERTIES:**
Colorless, saltlike compound, comparatively stable in air.

**REFERENCE:**
The following compounds may be prepared in a similar way:

\([\text{ClPy}_x\text{NO}_3]\), \([\text{BrPy}_x\text{NO}_3]\), \([\text{BrPy}_x\text{ClO}_4]\), \([\text{IPy}_x\text{NO}_3]\), \([\text{IPy}_x\text{ClO}_4}\)

(Py = \(\text{C}_5\text{H}_5\text{N}; x = 1\) or 2).


\([\text{IPy}_2\text{F}], [\text{BrPy}_2\text{F}]\).


**Bromine (III) Nitrate**

\(\text{Br(NO}_3\text{)}_3\)

\[
\text{BrF}_3 + 3 \text{N}_2\text{O}_5 = \text{Br(NO}_3\text{)}_3 + 3 \text{NO}_2\text{F}
\]

136.9 324.0 265.9 195.0

About 2 to 3 g. of \(\text{BrF}_3\) is distilled into a quartz receiver (trap) in high vacuum. About 40 ml. of Freon 11 (CFC1\(_3\)) is condensed on the \(\text{BrF}_3\), which has deposited on the receiver walls. After releasing the vacuum, the solvent is warmed to about \(-10^\circ\text{C}\) and the \(\text{BrF}_3\) melted into the Freon 11 by hand warming. Part of the \(\text{BF}_3\) dissolves, coloring the solution a pale yellow, and part of it forms a fine crystalline suspension. The \(\text{BF}_3\)-Freon solution (or suspension) is frozen with liquid nitrogen and a slight excess of finely pulverized \(\text{N}_2\text{O}_5\) is added through a tube attached to the receiver and protected against moisture. The liquid nitrogen is replaced by a bath kept at \(-30^\circ\text{C}\). This temperature is maintained for several hours, during which it is best to stir the mixture magnetically with a Teflon-coated stirrer. After this, the Freon and \(\text{NO}_2\text{F}\) are distilled off in high vacuum at \(-78^\circ\text{C}\). The \(\text{NO}_2\text{F}\) can be condensed in a receiver cooled with liquid nitrogen and the Freon in a receiver cooled to \(-140^\circ\text{C}\). The excess \(\text{N}_2\text{O}_5\) is sublimed off at \(-40^\circ\text{C}\) in high vacuum, the sublimation taking several hours. Pale yellow \(\text{Br(NO}_3\text{)}_3\) remains in vessel.

**Properties:**

White to pale yellow solid; very sensitive to moisture; slowly decomposes above 0°C into \(\text{Br}_2\), \(\text{O}_2\) and \(\text{NO}_2\). M.p. 48°C (dec.); soluble in Freon 11 and \(\text{CCl}_4\).

**Reference:**

Iodine (III) Nitrate
I(NO₃)₃

I.

$$\text{ICl}_3 + 3 \text{ClNO}_3 = \text{I(NO}_3)_3 + 3 \text{Cl}_2$$

233.3 292.4 312.9 212.8

An excess of ClNO₃ is condensed onto liquid-nitrogen-cooled IC₁₃ in high vacuum. After releasing the vacuum the mixture is warmed to 0°C. The reaction starts at −30°C, with evolution of chlorine. The products are allowed to stand for a day at 0°C and the insoluble cake that forms during this time is periodically broken up with a glass rod.

At the end of the 24-hour period, the unreacted C₁N₀₃ and the traces of Cl₂ are distilled off in high vacuum at −70°C.

II.

$$\text{ICl}_3 + 3 \text{HNO}_3 = \text{I(NO}_3)_3 + 3 \text{HCl}$$

233.3 189.1 312.9 109.5

Iodine (III) nitrate may also be prepared by treating IC₁₃ with anhydrous HNO₃.

By long and vigorous mixing with a magnetic stirrer, IC₁₃ is made into a slurry with Freon. An excess of a solution of anhydrous HNO₃ in Freon is then added drop by drop. A yellow, emulsion-like product is formed which can, to a large degree, be separated as flakes by cooling to −78°C. After settling and decanting the supernatant liquid, all volatile fractions are distilled off at −80°C in high vacuum. In order to remove the HNO₃ completely, the reaction mixture must remain in high vacuum overnight. During this time the temperature of the cold bath should rise to about −45°C. A yellow powder of I(NO₃)₃ remains in the flask.

PROPERTIES:

Yellow, brittle, hygroscopic solid; decomposes above 0°C with softening.

REFERENCES:


Iodine (III) Sulfate
I₂(SO₄)₃

Basic and neutral salts are among the compounds containing positive trivalent iodine. The colorless neutral salts are extremely
moisture sensitive, while the yellow basic compounds containing
the iodosyl group $\text{IO}^+$ are relatively stable.

$$(\text{IO})_2\text{SO}_4 \cdot \text{H}_2\text{O} + 3 \text{SO}_3 = \text{I}_2(\text{SO}_4)_3 + \text{H}_2\text{SO}_4$$

Sulfur trioxide ($40-50\ \text{g}$.) is distilled onto $10\ \text{g}$ of $(\text{IO})_2\text{SO}_4 \cdot \text{H}_2\text{O}$ (see below) in a 50-cm.-long and 2-cm. diameter tube. The tube is then sealed off and heated in a paraffin-oil bath until the dark-yellow $(\text{IO})_3\text{SO}_4$ converts to a homogeneous, yellow crystalline mass. This requires about 140 hours at 100-120°C. The individual crystals may be readily seen in the tube as long as the latter is still warm and the excess $\text{SO}_3$ is still fluid. After cooling, the product is freed of $\text{SO}_3$ on a porous clay plate placed in a desiccator over $\text{H}_2\text{SO}_4$. The bright yellow $\text{I}_2(\text{SO}_4)_3$ crystals are extremely hygroscopic and instantly develop a black color on contact with moist air (separation of $\text{I}_2$).

REFERENCE:


Iodine (III) Perchlorate

$\text{I}(\text{ClO}_4)_3$

$$\text{I}_2 + 6 \text{HClO}_4 + 3 \text{O}_3 = 2 \text{I}(\text{ClO}_4)_3 + 3 \text{H}_2\text{O} + 3 \text{O}_2$$

Iodine (4 g.) and anhydrous $\text{HClO}_4$ are precooled separately in ice-salt baths and then mixed. A stream of $\text{O}_2$ containing about 8% ozone is introduced while the mixture is kept at 0°C. The gas stream must be absolutely dry and the reaction flask carefully protected against moisture (be careful in handling $\text{HClO}_4$: organic materials must not come in contact with it!). When the solution assumes a transparent greenish color, treatment with $\text{O}_3$ is interrupted and the reaction vessel is left to cool for half an hour in the ice-salt mixture. The greenish-yellow crystals are suction-filtered on a filter crucible protected from moisture by a $\text{CaCl}_2$ tube and are washed with some cold, anhydrous $\text{HClO}_4$.

PROPERTIES:

Extraordinarily moisture sensitive; even at room temperature undergoes internal oxidation. Must therefore be kept cold.

REFERENCE:

Iodine (III) Iodate

I(IO₃)₃ or I₄O₉

I.

\[ 2I₂ + 9O₃ = I₄O₉ + 9O₂ \]

507.7 432 651.7 288

A stream of O₂ containing about 8% ozone is passed through a U tube, the lower part of which contains iodine. The latter is heated until vaporized. The yellow I₄O₉ product is precipitated in an attached U tube filled with washed and dried glass wool. Contact with moisture must be very carefully avoided during the entire preparation.

A variation of this method, using CHCl₃ solution, was described by Fichter and Rohner.

II.

\[ 4HIO₃ (+H₃PO₄) = I₄O₉ + 2H₂O + \frac{1}{2}O₂ (+H₃PO₄) \]

703.7 651.7 36 16

Concentrated phosphoric acid (d. 1.7, 20 ml.) is dehydrated by heating in a large Pt crucible. After cooling, 8 g. of powdered HIO₃ is added in portions with stirring and the mixture is carefully heated. Oxygen is evolved, and after about 15 minutes iodine vapor is given off, imparting a yellow color to the reactants. Heating is then interrupted and the crucible is cooled in a vacuum desiccator over H₂SO₄. A white, pasty mass gradually forms. This is stirred with concentrated H₂SO₄ in order to work it up. When the precipitate has settled, the liquid is decanted, and the crystalline mass is dried on a porous plate in a vacuum desiccator.

Care should be taken to make sure that the substance does not come into contact with moist air during any of the above equations.

PROPERTIES:

Extremely hygroscopic, bright yellow solid; decomposes above 75°C with formation of I₂O₅ I₂ and O₂.

REFERENCES:

Oxiodine (III) Sulfate

\((\text{IO})_2\text{SO}_4 \cdot \text{H}_2\text{O}\)

I. 

\[2 \text{HIO}_3 + \text{H}_2\text{SO}_4 = 2(\text{IO})_2\text{SO}_4 \cdot \text{H}_2\text{O} + \text{O}_2 + \text{H}_2\text{O}\]

\[
\begin{array}{cccc}
351.9 & 98 & 399.9 & 32 & 18
\end{array}
\]

A stirred mixture of 6 g. of HIO\(_3\) and 20 g. of concentrated H\(_2\)SO\(_4\) is heated in a platinum dish. Oxygen evolves for a few moments and the mixture then assumes a yellowish-brown color. The heating of the mixture is then continued with a smaller flame until violet iodine fumes are observed. As soon as this occurs, heating is stopped and the product is cooled and left to stand for 5-6 days in a desiccator over concentrated H\(_2\)SO\(_4\). The liquid is then decanted from the crust of yellow crystals. The crystals are powdered, washed with a small quantity of the decanted liquid, suction-filtered through fritted glass, and dried on a porous plate in a vacuum desiccator over H\(_2\)SO\(_4\). The yield is 5 g.

II. 

\[\text{I}_2 + \text{H}_2\text{SO}_4 + 3 \text{O}_2 = (\text{IO})_2\text{SO}_4 \cdot \text{H}_2\text{O} + 3 \text{O}_2\]

\[
\begin{array}{cccc}
253.8 & 98 & 144 & 399.8 & 96
\end{array}
\]

Iodine is dissolved in H\(_2\)SO\(_4\) and ozone-containing O\(_2\) is introduced, whereupon a yellow crystalline powder precipitates. It is treated as in method I.

PROPERTIES:

Yellow, hygroscopic powder, very slightly soluble in cold water. Hydrolysis yields I\(_2\), HIO\(_3\) and H\(_2\)SO\(_4\).

According to Chrétien, the compound has the formula \((\text{IO})_2\text{SO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}\); according to the more recent work of Bahl and Partington, the formula is \((\text{IO})_2\text{SO}_4 \cdot \text{H}_2\text{O}\). Bahl and Partington consider the product of the reaction of H\(_2\)SO\(_4\) with HIO\(_3\) as a mixture of \((\text{IO})_2\text{SO}_4 \cdot \text{H}_2\text{O}\) with \((\text{I}_2\text{O}_4) \cdot \text{H}_2\text{SO}_4\). However, when treated with a small amount of water, both compounds finally end up as I\(_2\)O\(_4\), since the HIO\(_3\) formed in the hydrolysis yields I\(_2\)O\(_4\) with \((\text{IO})_2\text{SO}_4 \cdot \text{H}_2\text{O}\). Also known as iodosyl sulfate.

REFERENCES:

Diiodine Tetroxide

\[ \text{IO} \cdot \text{IO}_3 \text{ or } \text{I}_2\text{O}_4 \]

\[ 4 \text{HIO}_3 = 2 \text{I}_2\text{O}_4 + \text{O}_2 + 2 \text{H}_2\text{O} \]

The tetroxide \( \text{I}_2\text{O}_4 \) is formed through the following intermediate reaction steps:

\[ 2 \text{HIO}_3 + \text{H}_2\text{SO}_4 = (\text{IO})_2\text{SO}_4 \cdot \text{H}_2\text{O} + \text{O}_2 + \text{H}_2\text{O} \]

\[ (\text{IO})_2\text{SO}_4 \cdot \text{H}_2\text{O} + 2 \text{HIO}_3 = 2 \text{I}_2\text{O}_4 + \text{H}_2\text{SO}_4 + \text{H}_2\text{O}, \]

where the \( \text{HIO}_3 \) appearing on the left side of equation (2) is formed from \((\text{IO})_2\text{SO}_4 \cdot \text{H}_2\text{O}\).

A sample of \((\text{IO})_2\text{SO}_4 \cdot \text{H}_2\text{O}\) obtained from \(\text{HIO}_3\) and \(\text{H}_2\text{SO}_4\) (see above) is tested to see whether iodine separation takes place when it is shaken with a small amount of \(\text{H}_2\text{O}\). If any \(\text{I}_2\) separates, the substance is left in the desiccator for a little longer time; if the test shows no iodine, the entire quantity is quickly washed several times with small amounts of water in a fritted glass suction filter until the wash water is free of sulfate. Suction is applied after each washing. The material is then washed with small amounts of absolute alcohol and then with absolute ether. The substance is dried at room temperature on a clay dish placed in a desiccator over calcium oxide.

**PROPERTIES:**

Formula weight 317.84. Lemon yellow crystals, not hygroscopic. Very slightly soluble in water. Hydrolysis yields \(\text{I}_2\) and \(\text{HIO}_3\). At 130°C, \(\text{I}_2\text{O}_4\) decomposes to \(\text{I}_2\text{O}_5\) and \(\text{I}_2\). \(d\) 4.2.

**REFERENCES:**

