Sulfur, Selenium, Tellurium

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Sulfur

S

PURE SULFUR

Commercial sulfur can be purified to a considerable extent by repeated recrystallization from CS$_3$.

A solution of 31.5 g. of S in 70 g. of CS$_2$ (C.P.) is prepared at room temperature. The solution is filtered and allowed to stand in ice for some time in a closed Erlenmeyer flask. The sulfur precipitate is filtered off and again crystallized several times in the same manner. At the end of this procedure, it is pressed between filter papers to remove all adhering solvent, and is finely pulverized and dried for a few hours at 90 to 100°C. The purified product is bright light-yellow, and retains only a very weak odor of CS$_2$.

However, R. F. Bacon and R. Fanelli claim that the material thus purified, as well as all "chemically pure" commercial sulfurs, are still contaminated with organic substances (particularly liquid hydrocarbons) as well as H$_2$S, H$_3$Sx and adsorbed gases. The only method capable of removing these stubbornly adhering impurities proceeds as follows:

One kilogram of sulfur is melted in a one-liter, short-neck glass flask on an open flame. During this operation, the flask is covered with an inverted fritted glass crucible. The temperature is slowly increased until the mass begins to foam. As soon as gas evolution subsides, the liquid is heated to boiling, 5 g. of pure MgO is added, and the solution is boiled for 3-4 hours. It is then allowed to stand at 125°C overnight. During this time a black sludge settles to the bottom of the flask; this is rapidly separated, together with the MgO, by filtration through a layer of glass wool. The clear filtrate is treated four more times in the same manner, i.e., each time adding 1% MgO, boiling for 25-30 hours, and filtering through glass wool. After a total treatment time of 100-120 hours, the filtrate is
very slowly cooled. The freshly purified product is completely gas free. After standing for several days in air, it is again partially contaminated with gases but can be readily degassed by repeated melting and solidifying at a pressure of 1 mm.

The progress of purification can be followed by occasionally testing the condensate collected on the covering frit. Thus, 3 g. of this sulfur is slowly heated to boiling in a Pyrex test tube (95 x 10 mm.) (with particular care being taken that the region of the high-viscosity melt is not traversed too quickly), boiled for 2-3 minutes, and allowed to cool and solidify. No black spots should appear at the lower walls of the glass which are in contact with the flame. The test is good to less than $10^{-4}$% impurities. Before the test, the test tube must be rinsed with hot cleaning solution, and during the test it must be protected from dust.

Von Wartenberg describes a simple method for obtaining S with a C content of less than $10^{-6}$%. This procedure requires no special attention and takes place over a period of a few days. A quartz tube, electrically heated to 750°C, is suspended in recrystallized boiling S, thus causing CS$_2$ to form on it. When no further black material precipitates on the tube, the sulfur is distilled in vacuum.

According to Skjerven, H$_2$S may be removed from this carbon-free sulfur by treatment with SO$_2$.

**PROPERTIES:**

Very pure sulfur is light yellow and completely odorless; the melt tends to supercool; there is no residue after burning or distilling.

**REFERENCES:**


**PLASTIC SULFUR**

Plastic sulfur is formed by rapid cooling of molten sulfur. Pure S is heated to 250-350°C under a nitrogen blanket. A thin stream of the melt is then poured into a cylindrical vessel (at least 60 cm. high) which has a bottom inlet and top outlet for ice-water flow. Strands of plastic sulfur collect in the lower part while the flowers of sulfur forming on the water surface are continuously flushed away.
Properties:

Yellow, plastic, viscoelastic, amorphous mass. The strands can be stretched out to many times their initial length, which causes partial crystallization. Repeated stretching produces loss of elasticity. More detailed studies have been made by K. Sakurada and H. Erbring, Kolloid-Z. 72, 129 (1935). Insoluble in water, partially soluble in CS₂.

References:


Colloidal sulfur solution

I. A very stable monodispersed S sol is obtained by mixing acidified Na₂S and Na₂SO₃ solutions of the proper concentration, followed by peptization.

Solutions of 7.2 g. of C.P. Na₂SO₃ · 7H₂O and 64 g. of C.P. Na₂S · 9H₂O, each in 50 ml. of distilled H₂O, are prepared separately. Then 1.5 ml. of the Na₂SO₃ solution is added with a pipette to the Na₂S solution. A mixture of 10 ml. of distilled H₂O and 2.7 g. of concentrated H₂SO₄ is then added in drops with constant stirring up to the point of incipient turbidity (a total of 8 ml. is needed). Then 5.5 g. of concentrated H₂SO₄ is added to the remaining Na₂SO₃ solution and the Na₂S solution is poured in with constant stirring. The mixture is allowed to stand for one hour in an Erlenmeyer flask covered with a watch glass. It is then filtered through a fluted funnel; the precipitate is washed from the outside of the filter with about 100 ml. of H₂O and is peptized on the filter with 300 ml. of distilled water. About 5 to 10 ml. of the yellowish-white colloidal sulfur solution running through the filter is poured into 300 ml. of distilled H₂O, forming a beautiful, reddish opalescent sulfur sol. After 24 hours the slight deposit of solid which may have formed is filtered off. The sol is then stable for weeks.

II. More highly concentrated S sols may be obtained by peptization of finely divided S precipitates in the presence of a protective colloid.

After the S precipitate on the fluted funnel, prepared according to method I, has been washed, it is mixed with sufficient 10% agar solution and dilute NaOH to reach a concentration of 0.6% agar and 0.4% NaOH in the sol product, relative to the weight of dry sulfur. The mixture is then decanted from the insoluble components. The resulting sol is very stable.
REFERENCES:
I. A. Janek, Kolloid-Z. 64, 31 (1933).
II. British Pat. 411 241 (1934), IG. Farbenindustrie.

Hydrogen Sulfide

$\text{H}_2\text{S}$

The hydrogen sulfide gas prepared in the laboratory from FeS and dilute HCl is generally contaminated with acid vapors such as $\text{H}_2$, $\text{CO}_2$, $\text{AsH}_3$, $\text{N}_2$ and $\text{O}_2$. The HCl can be readily removed by scrubbing with distilled water. To remove $\text{AsH}_3$, Jacobsen recommends that the gas, predried with $\text{CaCl}_2$, be passed through a U tube containing dry iodine and glass wool. The As deposits as $\text{AsI}_3$ and the simultaneously formed HI is then scrubbed out with distilled water. After drying with $\text{P}_2\text{O}_5$, the permanent gases $\text{H}_2$, $\text{N}_2$ and $\text{O}_2$ can be removed by condensing the $\text{H}_2\text{S}$ in a trap cooled with Dry Ice freezing mixture.

A considerably purer gas is obtained by the decomposition of CaS (prepared by the Otto method and pressed into cubes) with very pure dilute hydrochloric acid. The product gas is passed through a wash bottle with distilled water, two wash bottles with KHS solution, a U tube with $\text{CaCl}_2$, and finally, into a trap cooled with Dry Ice mixture. The $\text{H}_2\text{S}$ reevaporated from this trap is contaminated only with a small quantity of $\text{CO}_2$.

Very pure, air- and $\text{CO}_2$-free $\text{H}_2\text{S}$ can be prepared via the following procedures:

I. HEATING OF CONCENTRATED $\text{Mg(HS)}_2$ SOLUTION

A one-liter round-bottom flask with a two-hole rubber stopper serves as the gas generator. A separatory funnel (250 ml.) and a gas outlet tube are placed in the stopper. Then 250 ml. of saturated $\text{MgCl}_2$ solution is allowed to flow in from the separatory funnel, followed by the same quantity of $\text{H}_2\text{O}$, and finally, by the same volume of saturated NaHS solution. A uniform $\text{H}_2\text{S}$ stream is generated on slight heating of the flask. The gas is free of $\text{CO}_2$. At the beginning of the run, the apparatus is flushed with nascent $\text{H}_2\text{S}$ (use a hood!) until all the air is displaced. After this, the gas is very pure. It is dried over $\text{P}_2\text{O}_5$ and glass wool and can be used for most laboratory purposes. The yield, based on hydrosulfide, is about 80%.

II. $\text{H}_2 + \text{S} = \text{H}_2\text{S}$

2.02 32.07 34.09

Especially pure $\text{H}_2\text{S}$ can be obtained by synthesis from the elements. The apparatus is shown in Fig. 153. The flask $R$, made
of high-melting glass, is charged with about 250 g. of carefully purified S (see p. 341). The side arm reaction tube r–b, inclined upward and having an internal diameter of 2.5 cm. and a length of 150 cm., is filled with pea size pumice chips for a length of 80 cm. These are prepurified by boiling with concentrated HCl, dilute H$_2$SO$_4$ and then H$_2$O until they show no Cl$^-$ or SO$_4^{2-}$ reaction. They are then calcined in a nitrogen and then in a hydrogen stream. The part of the tube containing the chips is encased in furnace E and can be heated to 600°C. A lead cooling coil is wound around the middle of the tube section that protrudes from the furnace. The tube outlet is closed off with a thick wad of absorbent cotton and a one-hole rubber stopper. From the stopper, a tube leads to the purification and condensation setup (wash bottle 1 contains distilled water; wash bottles 2 and 3: distilled water and glass chips; wash bottle 4: absorbent cotton).

Fig. 153. Preparation of hydrogen sulfide.

At the beginning of the run, carefully purified N$_2$ is introduced at E until the air is completely displaced from the apparatus. Then H$_2$ is allowed to flow in at a rate of 8–9 liters/hour, while E is switched on. When the temperature has risen to 600°C, A$_1$ is cooled with liquid nitrogen and the sulfur in B is heated to boiling. The hydrogen reacts quantitatively to form H$_2$S. The heat input at R should be regulated in such a way that no sulfur accumulates in the side arm and a deposit of flowers of sulfur is formed on the cotton wad only after some time has elapsed. A loose condensate of long, shiny H$_2$S crystals precipitates in A$_1$. It is melted briefly from time to time in order to utilize the condenser volume completely and to avoid plugging of the inlets and outlets. When A$_1$ is full, stopcock a is opened and A$_1$ is sealed at c. For purification the material is distilled from A$_1$ into A$_2$ in a high vacuum by slowly heating A$_1$ and cooling A$_2$ with liquid nitrogen (the intermediate U tubes are cooled with Dry Ice mixture). The first and last portions of the distillate are discarded. About 130 liters of H$_2$S
are obtained in 18 hours; the impurity content of the gas is less than 0.01%.

III. Pure \( \text{H}_2\text{S} \), completely free of hydrochloric acid, is obtained in a simple manner by decomposition of a concentrated aqueous solution of C.P. \( \text{Na}_2\text{S} \cdot 9\text{H}_2\text{O} \) with 20-30% phosphoric acid (C.P.). The acid is allowed to drip slowly from a separatory funnel into the sodium sulfide solution, and the evolving gas is dried over \( \text{CaCl}_2 \) and \( \text{P}_2\text{O}_5 \).

Hydrogen sulfide is stored in liquid form at low temperature or in gasometers over saturated \( \text{NaCl} \) solution. Mercury may also be used as sealing fluid when the gas is completely pure and dry.

**PROPERTIES:**

Colorless gas with an unpleasant odor reminiscent of rotten eggs; highly toxic. Reducing agent for many substances; for this reason \( \text{H}_2\text{S} \) cannot be dried with concentrated \( \text{H}_2\text{SO}_4 \).

M.p. \(-83^\circ\text{C}\), b.p. \(-59^\circ\text{C}\), crit. t. \(+100.5^\circ\text{C}\), crit. p. 98.0 atm. gage; d (b.p.) 0.9504; wt. per liter 1.5392 g. Solubility at 760 mm. in 1 volume of \( \text{H}_2\text{O} \) (0°C): 4.67; (20°C): 2.58; (100°C): 0.81 volume of \( \text{H}_2\text{S} \); for further details, see D'Ans-Lax (1949), Table 332632 A, 7, p. 970; also soluble in ethanol.

In crystalline \( \text{H}_2\text{S} \), the S atoms form a face-centered cubic lattice; probably type C1 or C2.

**REFERENCES:**


**Crude Sulfane**

\( \text{H}_2\text{S}_x \)

I.

\[
\text{Na}_2\text{S} + y \text{S} = \text{Na}_2\text{S}_x \quad (x = y + 1)
\]

\[
\text{Na}_2\text{S}_x + 2 \text{HCl} = \text{H}_2\text{S} + 2 \text{NaCl}
\]

An aqueous solution of sodium polysulfide with the approximate composition \( \text{Na}_2\text{S}_{5.5} \) serves as the starting material. It is
prepared as follows: A two-liter, round-bottom, long-neck flask is placed on a steam bath and filled with 500 g. of \( \text{Na}_2\text{S} \cdot 9\text{H}_2\text{O} \), which is then heated with 250 g. of powdered \( \text{S} \) for three hours. Frequent shaking is necessary. The sulfide melts in its water of crystallization and dissolves most of the sulfur, with the color of the mixture becoming deeper. The cooled, dark red-brown solution is diluted with 400 ml. of \( \text{H}_2\text{O} \). It is then rapidly suction-filtered to remove \( \text{S} \) residue and other impurities, and the filtrate is diluted with water to one liter.

Next, a five-liter filtration jar is thoroughly cooled on the outside with an ice-salt mixture, and 2 kg. of finely crushed ice and two liters of pure concentrated hydrochloric acid (d 1.19) are added one after the other. When the acid reaches a temperature of \(-15 \text{ to } -20^\circ\text{C}\), the addition of \( \text{Na}_2\text{S}_x \) solution is begun. The solution (in a separatory funnel) is added with thorough stirring over a period of 1-1.5 hours. The solution becomes cloudy during the reaction because of the formation of a milky-white sulfur emulsion. The \( \text{H}_2\text{S}_x \) product settles at the bottom as a yellow oil. The addition rate should be so controlled that the temperature does not rise above \(-10^\circ\text{C}\), if at all possible, and in no case above \(-5^\circ\text{C}\); otherwise, decomposition of the \( \text{H}_2\text{S}_x \) and evolution of \( \text{H}_2\text{S} \) occurs. After all the \( \text{Na}_2\text{S}_x \) solution has been added and the product oil has completely settled, the mother liquor is decanted and the oil is washed in the filtration jar with 1 N \( \text{HCl} \) and decanted in a separatory funnel. A small quantity of \( \text{P}_2\text{O}_5 \) is added to the crude sulfane. The product has the approximate composition \( \text{H}_2\text{S}_{5-6} \); it can be stored in a closed glass vessel at \( 0^\circ\text{C} \) for a fairly long period without change. Before further use, the \( \text{P}_2\text{O}_5 \) is filtered off through glass wool. Freshly prepared \( \text{H}_2\text{S}_x \) should form a clear solution with pure benzene. The yield is 260 g. (160 ml.) of oil, i.e., 87% relative to the starting sulfur.

If crude sulfane is to be prepared continuously in fairly large quantities, the apparatus described by F. Fehér and W. Laue should be used.

Use of sulfane for the preparation of \( \text{H}_2\text{S}_2 \) and \( \text{H}_2\text{S}_3 \): A crude sulfane which is especially rich in \( \text{H}_2\text{S}_4 \) and is therefore suited for the production of tetrasulfane is prepared in the following manner:

A solution of \( \text{Na}_2\text{S}_2 \) is prepared by heating 480 g. of \( \text{Na}_2\text{S} \cdot 9\text{H}_2\text{O} \), 64 g. of powdered \( \text{S} \) and 500 ml. of \( \text{H}_2\text{O} \) for three hours in a two-liter round-bottom flask on a steam bath. The cooled solution, suction-filtered to remove \( \text{S} \) residues, is then decomposed in the manner described above, using four liters of dilute \( \text{HCl} \). The yield is 32 ml. of crude sulfane having the approximate composition \( \text{H}_2\text{S}_{5-6} \).

Il. In general, excess sulfane, \( \text{H}_2\text{S}_n \), which also acts as a solvent, reacts with a chlorosulfane \( \text{S}_m\text{Cl}_2 \), producing quantitative \( \text{HCl} \).
separation and chain increase and forming a higher sulfane \( \text{H}_2\text{S}_{2n+m} \) according to the following scheme:

\[
\text{H—Sn—[H + Cl]—Sm—Cl + H—Sn—H = H}_2\text{S}_{2n+m} + 2\text{HCl}
\]

Excess \( \text{H}_2\text{S}_n \)

The \( \text{H}_2\text{S}_{2n+m} \), which is formed as an intermediate, reacts in turn with the \( \text{S}_m\text{Cl}_2 \). Again, \( \text{HCl} \) is split off. The formation of a homologous mixture of sulfanes (= crude sulfane, \( \text{H}_2\text{S}_x \)) is based on this fact. (See also p. 353).

The number of moles of reagents, \( a \) and \( b \), in the equation below gives the average composition \( x \) and the quantity \( c \) of crude sulfane formed when the quantity \( d \) of unreacted sulfane distilled off after the reaction is determined. The equation was derived on the basis of assumption about the molecular distribution obtained in the condensation of sulfanes and halosulfanes (F. Feher and W. Laue); however, it holds only for the above described reactions under the further restriction that no other reactions take place.

\[
a\text{H}_2\text{S}_n + b\text{S}_m\text{Cl}_2 = c\text{H}_2\text{S}_x + 2b\text{HCl} + d\text{H}_2\text{S}_n
\]

\[
x = \frac{am + n(2a - b)}{a - b};
\]

\[
c = \frac{b(n + m)}{x - n};
\]

\[
d = a(1 - \frac{b}{a})
\]

Interfering side reactions which lead to a higher \( S \) content of the crude sulfane are favored, among other things, by too violent a reaction and by too small a sulfane excess. Because of its ease of preparation, only \( \text{H}_2\text{S} \) (\( n = 1 \)) is of importance as a raw material for "crude oil." The reagents for the preparation of chlorosulfane are \( \text{SCl}_2 \) (\( m = 1 \)) and \( \text{S}_2\text{Cl}_2 \) (\( m = 2 \)). Elementary chlorine, which reacts very violently, may also be used. Since the product is either distilled or cracked, the formation of side products is of no particular importance.

For example, the reaction of a 7-mole excess of \( \text{H}_2\text{S} \) with \( \text{SCl}_2 \) yields a crude oil with the approximate composition \( \text{H}_2\text{S}_{4.5} \) and containing fairly large quantities of \( \text{H}_2\text{S}_3 \). With \( \text{S}_2\text{Cl}_2 \), a crude oil of the approximate composition \( \text{H}_2\text{S}_{5.2} \), containing a large amount of \( \text{H}_2\text{S}_4 \), is obtained. These reactions are carried out in the same apparatus and in a manner analogous to that described for the preparation of tetrasulfane (p. 354). The reaction of liquid \( \text{H}_2\text{S} \) with \( \text{Cl}_2 \) yields mainly \( \text{H}_2\text{S}_3 \) and \( \text{H}_2\text{S}_4 \), plus a small amount of \( \text{H}_2\text{S}_2 \).

The choice of the second component in the reaction with liquid \( \text{H}_2\text{S} \) usually depends either on the sulfane which is to be distilled directly from the crude mixture or, if cracking is to follow the primary reaction, on the composition of the sulfane mixture which is best suited for that process.
SYNONYMS:


PROPERTIES:

Yellow liquid resembling olive oil, pungent odor of camphor and S₂Cl₂.

No definite m.p.; solidifies in liquid air to form a glassy mass which softens again on heating over a fairly broad temperature range. On heating, cracking to lower hydrogen sulfides (see H₂S₂ and H₂S₃) takes place. Gradually decomposed by water with evolution of H₂S. Spontaneous decomposition is caused by alkalis and sometimes even by the alkali content of glass. For this reason, all vessels which come in contact with the product must be "neutralized" beforehand by rinsing with hot, concentrated hydrochloric acid or by treatment with gaseous HCl. Soluble in CS₂, C₆H₆ and CHCl₃.

REFERENCES:


Pure Sulfanes

Since sulfanes are readily decomposed by alkali, metals, dust, cork, rough surfaces and moisture, all glass vessels which come in contact with them (even glass wool) must be thoroughly cleaned, carefully dried and stored in a dust-free atmosphere.

Glass vessels are rinsed with hot cleaning solution, then with hot, pure, concentrated hydrochloric acid, and finally with distilled water. Apparatus contaminated with sulfur can be precleaned with CS₂ or hot ammonium sulfide solution.

Ground glass connections should be sealed with silicone grease. No NH₃ gas (e.g., from bottles of concentrated ammonia or ammonium sulfide in the area) may be present in the atmosphere.
All reactions with sulfanes must be protected from moisture, and pure starting materials must be used. These precautions must always be very carefully adhered to when working with sulfanes, even when this is not expressly pointed out in the preparation.

I. DISULFANE AND TRISULFANE, \( \text{H}_2\text{S}_2, \text{H}_2\text{S}_3 \)

Both of these hydrogen sulfide compounds are formed by cracking of crude sulfane, using the apparatus shown in Fig. 154.

\[
\text{H}_2\text{S}_x = \text{H}_2\text{S}_2 + (x-2)\text{S} \\
\text{H}_2\text{S}_x = \text{H}_2\text{S}_3 + (x-3)\text{S}
\]

Since the yields of \( \text{H}_2\text{S}_2 \) and \( \text{H}_2\text{S}_3 \) improve when only small quantities of \( \text{H}_2\text{S}_x \) are cracked at a time, the process is carried out as follows. First, flask \( a \) (300 ml.) is heated in a paraffin bath to 110°C while the apparatus is evacuated to 12-15 mm. Then 15 ml. of \( \text{H}_2\text{S}_x \) (see p. 346 for preparation) is introduced through \( d \). After a short time the condenser surface is coated with fine droplets. The \( \text{H}_2\text{S}_3 \) collects slowly but at a uniform rate in receiver \( b \), which is at room temperature, while the \( \text{H}_2\text{S}_2 \) is condensed in trap \( c \), which is cooled with Dry Ice-methanol mixture. Then the bath temperature at \( a \) is slowly increased to 125°C over a period of 20 minutes. The flask contents are cooled to 110°C and 15 ml. of \( \text{H}_2\text{S}_x \) is again added through \( d \). The 20-minute heating procedure is repeated. After two portions of \( \text{H}_2\text{S}_x \) have been cracked, the vacuum is released and air is slowly introduced into the apparatus, passing through the \( \text{CaCl}_2 \) and soda-lime tubes. The ground glass joint at \( a \) is then quickly disconnected, and the hot, still liquid

![Fig. 154. Preparation of di- and trisulfane.](image)
residue is poured out, whereupon it solidifies. After the ground glass joint has been resealed, the cracking is continued and the residue is again removed after two 15-ml. additions of \( \text{H}_2\text{S}_x \). About 25 ml. of \( \text{H}_2\text{S}_3 \) and 15 ml. of \( \text{H}_2\text{S}_2 \) are obtained from 120 ml. of freshly prepared \( \text{H}_2\text{S}_x \). With aged \( \text{H}_2\text{S}_x \), the yield of \( \text{H}_2\text{S}_2 \) increases, while that of \( \text{H}_2\text{S}_3 \) is reduced. Both products are nearly pure; at most, each is contaminated by a small amount of the other.

Use of the Bloch and Höhn suction device to remove the cracking residue is not recommended since the residue solidifies easily in the narrow tubes and is then difficult to remove.

Fig. 155. Distillation of disulfane.

The disulfane is further purified by distillation in the apparatus shown in Fig. 155.

The low-temperature column \( k \) is a Liebig condenser filled with glass Raschig rings. It is cooled by circulating methanol from a constant temperature bath \( t \). The distillation flask \( d \) is placed in a water bath \( w \) at room temperature. The trap \( f \) for collecting the pure disulfane is attached to \( k \) with an adapter. The liquid-nitrogen-cooled double trap \( l \) is connected to a vacuum pump.

After the crude disulfane, which has been dried with \( \text{P}_2\text{O}_5 \) and filtered through glass wool, is charged into the distillation flask \( d \), the column is cooled to \(-15^\circ\text{C}\) and the system is slowly evacuated to 15 mm. The flask contents foam vigorously, releasing the dissolved \( \text{H}_2\text{S} \). When the initial foaming subsides, condensation of the pure disulfane is begun by cooling \( f \) with a Dry Ice-methanol mixture. Further distillation does not require any special attention.

Purification of 100 g. of disulfane takes about 1.5 hours.

The trisulfane is further purified by distillation in the apparatus shown in Fig. 156.

The 500-ml. flask \( d \), immersed in water bath \( w \), carries a Liebig condenser \( k \), filled with glass Raschig rings and a spiral
condenser $\kappa_2$. The latter expands at the bottom to a toroid, from which an outlet leads to receiver $v$. A horizontal connecting tube leads from $\kappa_2$ to trap $f$. The latter is followed by double trap $l$, cooled with liquid nitrogen, and this in turn is connected to a high-vacuum pump. Each condenser is provided with its own constant-temperature circulation system. The run is started by adjusting the temperature in $\kappa_1$ to 42°C. Then flask $d$ is filled with the crude trisulfane and attached to the apparatus. Trap $f$ is cooled with Dry Ice-methanol and the system is slowly evacuated. When a pressure of 1.5 mm. is reached, $\kappa_2$ and $v$ are cooled with ice water and water bath $w$ is heated to 52°C. The distillation now proceeds without further attention; $H_2S_3$ condenses in $v$. The more volatile oils condense in $f$ and the less volatile components in $\kappa_1$, from which they flow back into flask $d$. The temperatures in $\kappa_1$, $\kappa_2$ and $w$ must be constant during the run. The pure distillate generally has the composition $H_2S_3.00-3.03$.

Equipment for the continuous preparation of larger quantities of $H_2S_2$ and $H_2S_3$ is described by F. Fehér and M. Baudler, Z. anorg. Chem. 253, 170 (1947); 254, 251 (1947); and F. Fehér, W. Laue and G. Winkhaus, Z. anorg. allg. Chem. 288, 113 (1956). This
equipment may also be used to prepare disulfane in yields greater than those described above.

II. TETRASULFANE, $\text{H}_4\text{S}_4$

Tetrasulfane is obtained from crude sulfane in the apparatus shown in Fig. 157.

The modified Utzinger tube $h$, the lower part of which is flattened to increase the vaporization surface as much as possible (see cross section), is surrounded by a heating jacket and carries a separatory funnel $t$ and a 500-ml. flask $r$. The attached condenser $\kappa_1$ and the spiral condenser $\kappa_2$ (which is identical to that used in trisulfane purification and has a toroidal expansion and an outlet to the receiver $v$) are provided with separate constant-temperature circulating systems. Again, condenser $\kappa_2$ is connected to trap $f$, which is immersed in a Dry Ice-methanol mixture. Trap $f$ adjoins double trap $l$, cooled with liquid nitrogen, which is connected to a high-vacuum pump. The connecting sections of the condensers are covered with asbestos insulation $i_1$ and $i_2$.

The system is evacuated until a pressure of $10^{-3}$ mm is attained. Tube $h$ is heated to 75°C, $\kappa_1$ to 50°C, and $\kappa_2$ and the water bath to 15°C. Then crude oil of composition $\text{H}_3\text{S}_4$ (preparation on p. 346) is allowed to drip slowly from the separating funnel $t$ into the tube $h$. The volatile components of the oil distill off while the residue collects in $r$. Condenser $\kappa_2$ separates the tetrasulfane from the lighter and heavier components of the distillate. The product is collected in $v$. An $\text{H}_2\text{S}_3$-$\text{H}_3\text{S}_3$ mixture collects in $f$ while the higher-boiling fractions flow from $\kappa_1$ into $r$.

III. TETRA-, PENTA-, HEXA-, HEPTA- and OCTASULFANES

$\text{H}_4\text{S}_4$, $\text{H}_5\text{S}_5$, $\text{H}_6\text{S}_6$, $\text{H}_7\text{S}_7$, $\text{H}_8\text{S}_8$

$$(a - 2)\text{H}_2\text{Sn} + \text{H} - \text{Sn} - \text{Cl} - \text{Cl} - \text{H} - \text{H} =$$

$$\text{H}_2\text{S}_{2n + m} + 2\text{HCl} + (a - 2)\text{H}_2\text{Sn}$$

$n = 1, 2$.
$m = 1, 2, 3, 4, 5, 6$.

In general, excess sulfane $\text{H}_2\text{Sn}$ reacts with a chlorosulfane $\text{S}_m\text{Cl}_2$, splitting off HCl quantitatively and polymerizing to form a homologous mixture of chain sulfanes. The formation of such a mixture is predicated on the fact that the product of the primary reaction reacts further with the chlorosulfane (compare p. 348).

If, however, a very large excess of the $\text{H}_2\text{Sn}$ component $(a)$ is used, individual sulfanes can be obtained via direct synthesis. In this case, the rate of formation of the sulfane is so much larger than that of the homologs that it is reaction-controlling. The excess of the sulfane, $(a - 2)\text{H}_2\text{Sn}$, is distilled off after the reaction. Using this principle, it is possible to obtain, with appropriate chloro-
sulfanes, almost pure $H_2S_4$, $H_2S_5$, $H_2S_6$, $H_2S_7$ and $H_2S_8$. The preparative procedures for all these products are analogous, the reaction conditions mild, and the products almost uncontaminated with each other.

These sulfanes are generally best prepared from the following reactants:

<table>
<thead>
<tr>
<th>Desired sulfane</th>
<th>Sulfane component</th>
<th>Chlorosulfane component</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2S_4$</td>
<td>$H_2S$</td>
<td>$S_2Cl_2$</td>
</tr>
<tr>
<td>$H_2S_5$</td>
<td>$H_2S_2$ or $H_2S$</td>
<td>$SCl_2$ or $S_3Cl_2$</td>
</tr>
<tr>
<td>$H_2S_6$</td>
<td>$H_2S_2$ or $H_2S$</td>
<td>$S_2Cl_2$ or $S_3Cl_2$</td>
</tr>
<tr>
<td>$H_2S_7$</td>
<td>$H_2S$</td>
<td>$S_3Cl_2$</td>
</tr>
<tr>
<td>$H_2S_8$</td>
<td>$H_2S_2$</td>
<td>$S_4Cl_2$</td>
</tr>
</tbody>
</table>

As an example of the procedure and the ratios of the reactants used, the preparation of tetra- and pentasulfane are described.

a) TETRASULFANE, $H_2S_4$

$$H-S-H + Cl-S-Cl + H-S-H = H_2S_4 + 2HCl$$

Excess $H_2S$

The reaction is carried out in a 500-ml., four-neck flask, provided with one male and three female ground glass connections for $P_2O_5$ drying tube, separating funnel, low-temperature thermometer, and a mercury seal stirrer. The product is poured out through the neck with the male connection.

To prepare the $H_2S$, a concentrated aqueous solution of C.P. Na$_2$S $\cdot$ 9H$_2$O (1800 g.) is decomposed with C.P. 25% H$_3$PO$_4$ (3400 g.) (compare p. 346) and the gas is passed through CaCl$_2$ and $P_2O_5$ drying tubes into a cooled trap (methanol-Dry Ice) where about 150 ml. of $H_2S$ is condensed. From this trap, the $H_2S$ is distilled into the reaction flask, passing through the CaCl$_2$ and $P_2O_5$ drying tubes. The reaction flask is immersed in a Dewar flask containing Dry Ice-methanol mixture and the gas is thus liquefied.

About 20 g. of dichlorodisulfane (about 0.15 mole) is carefully added from a separatory funnel. The addition temperature is $-80^\circ C$, stirring is employed, and the dichlorosulfane is added drop-by-drop over a period of two hours. It is advisable to precool the chlorosulfane. Thus, a bent capillary is attached to the outlet tube of the separatory funnel. This capillary is immersed in the liquid $H_2S$ and then discharges above the surface of the $H_2S$. The reaction
is complete after about 12 hours, when the reaction mixture has become colorless. The excess H₂S, contaminated with HCl, is slowly evaporated by removing the Dewar flask. The last traces of H₂S are removed by briefly applying an aspirator vacuum. Clear, almost pure tetrasulfane remains in the flask. Since H₂S is highly toxic, the preparation must be carried out under a good hood.

b) PENTASULFANE, H₅S₅

\[
\begin{align*}
\text{H—S—[H + Cl]—S—Cl + H} & \rightarrow \text{H₅S₅} \text{—H} = \text{H₅S₅ + 2HCl} \\
66.15 & \quad 102.98 & \quad 66.15 & \quad 162.35 & \quad 72.93
\end{align*}
\]

Excess H₂S₂

The reaction flask (described in the preparation of tetrasulfane; see above) containing 100 g. H₂S₂ is cooled with Dry Ice-methanol to −60 to −65°C in a Dewar flask. From the separatory funnel, 10 g. of SCl₂ (about 0.1 mole) is allowed to drip in slowly (with stirring) in such a way that the temperature of the mixture does not rise above −55°C. In contrast to the preparation of tetrasulfane, the use of a bent outlet capillary is not recommended, since it plugs easily. The Dewar flask is removed 15 minutes after the completion of the dropwise addition. When the mixture has warmed to 0°C, the temperature is held constant until the evolution of HCl has, for all practical purposes, ended; the mixture is then stirred for another 0.5 hour at room temperature. The total reaction time is 1.5 hours.

The clear mixture is poured into a 250-ml., two-neck flask. One neck of this flask, the one connected to a receiving trap, is shaped as shown in Fig. 158. This intricate shape is necessary since the H₂S₂ to be evaporated tends to superheat and splash. The other neck is a male ground glass piece and is used for pouring out the product. Most of the H₂S₂ is removed in a vacuum of 15 mm., the remainder in high vacuum (about 10⁻³ to 10⁻⁴ mm.). The product is also briefly heated to 30 to 40°C during the last stage of H₂S₂ removal. The generally quite clear greenish-yellow to yellow residue represents the desired product, which is quite pure.

Fig. 158. Evaporation of excess disulfane.

PROPERTIES:

H₅S₅:

Formula weight 66.15. M.p. −89.6°C, b.p. 70.7°C; d. (20°C) 1.334. Light yellow liquid.
H₂S₃:
Formula weight 98.21. M.p. -52 to -54°C; d (20°C) 1.491. On heating, cracking to H₂S₂, H₂S₃ and S occurs. Light yellow liquid of somewhat deeper color than H₂S₂. Both H₂S₂ and H₂S₃ have a pungent odor of camphor and S₂Cl₂; the vapors are irritating to the eyes and mucous membranes. On prolonged standing, both are converted to homologs richer in sulfur, giving off H₂S. With water they decompose with evolution of H₂S and precipitation of S. Soluble in CS₂, C₆H₆ and CHCl₃.

H₂S₄:
Formula weight 130.28. Bright light-yellow liquid similar to olive oil, pungent odor. Somewhat less easily decomposed than H₂S₂ and H₂S₃; like these, it is converted on prolonged standing into homologs richer in sulfur. No definite melting point; solidifies at about -85°C to a white, glassy mass which gradually softens over a fairly wide temperature range when heated. Cracked by heating to lower hydrogen sulfides, particularly H₂S. d (20°C) 1.582.

H₂S₅:
Formula weight 162.35. d (20°C) 1.644.

H₂S₆:
Formula weight 194.41. d (20°C) 1.688.

H₂S₇:
Formula weight 226.48. d (20°C) 1.721.

H₂S₈:
Formula weight 258.54. d (20°C) 1.747.

The properties of the higher sulfanes (from H₂S₅ up) are similar to those of the lower homologs. They are greenish-yellow liquids, changing to a deeper yellow with increasing chain length. At 0°C, the substances are stable for several days if they are protected from contact with air.

REFERENCES:


**Ammonium Hydrogen Sulfide**

\[
\text{NH}_4\text{HS}
\]

\[
\text{NH}_3 + \text{H}_2\text{S} = \text{NH}_4\text{HS}
\]

17.03 34.08 51.11

Carefully dried \(\text{NH}_3\) and \(\text{H}_2\text{S}\) are alternately added to an Erlenmeyer flask containing anhydrous ether at \(0^\circ\text{C}\); the flask must be carefully protected from moisture. White crystals of pure \(\text{NH}_4\text{HS}\) precipitate. These readily decompose again at room temperature into \(\text{NH}_3\) and \(\text{H}_2\text{S}\) and must therefore be quickly suction-filtered and freed of adhering ether by pressing between filter papers. When sealed in glass ampoules, \(\text{NH}_4\text{HS}\) is stable for some time.

**Properties:**

White, needle-shaped crystals; easily decomposed; dissociation pressure at room temperature about 350 mm, \(d\ 1.17\).

Readily soluble in water and ethanol, forming colorless solutions which rapidly yellow in air; insoluble in ether and benzene.

Tetragonal crystals, space group \(D_{4h}\).

**Reference:**


**Sodium Hydrogen Sulfide**

\[
\text{NaHS}
\]

\[
\text{C}_2\text{H}_5\text{ONa} + \text{H}_2\text{S} = \text{NaHS} + \text{C}_2\text{H}_5\text{OH}
\]

68.06 34.08 56.07 46.07

Carefully dehydrated \(\text{C}_2\text{H}_5\text{OH}\) (20 ml.) and small, bright pieces of \(\text{Na}\) (2 g.) are placed in a 150-ml glass flask equipped with a reflux condenser and an adapter, closed at first, for introducing a gas
inlet tube. A drying tube on the reflux condenser prevents penetration of atmospheric moisture. When the ethoxide begins to separate, just enough additional C$_2$H$_5$OH is added to keep all solute in solution at room temperature. A total of about 40 ml. of C$_2$H$_5$OH is needed. Then a glass tube, reaching to the bottom of the flask, is introduced through the adapter and sealed in tightly with a rubber stopper or a piece of hose. A fast stream of pure, carefully dried H$_2$S (see p. 344 ff.) is introduced through this tube into the solution. After a few minutes, an abundant, fine crystalline precipitate of slightly impure NaHS separates out. The solution is saturated with H$_2$S and quickly suction-filtered. The filtrate is transferred into a dry Erlenmeyer flask and 50 ml. of pure absolute ether is added. A dense, pure white precipitate of NaHS separates immediately. It is allowed to settle in the stoppered flask, and small portions of ether are added as long as crystals continue to form in the supernatant liquid. In all, about 110 ml. of ether is required for the precipitation. The precipitate is quickly suction-filtered, washed with absolute ether, and transferred to a vacuum desiccator. The yield is 4.3 g. of NaHS. The product is almost analytically pure. Redissolution in absolute C$_2$H$_5$OH and reprecipitation with ether readily yields a completely pure substance.

PROPERTIES:

White, granular crystalline powder; very hygroscopic. Turns yellow on heating in dry air, orange at higher temperatures; melts to a black liquid at about 350°C. d 1.79.

Very soluble in water; moderately soluble in C$_2$H$_5$OH. Pure NaHS dissolves in hydrochloric acid with vigorous evolution of H$_2$S to form a clear solution. Aged products give a weakly yellowish, opalescent solution.

Rhombohedrally distorted NaCl structure, space group D$_3d^5$.

REFERENCES:


**Sodium Sulfide**

\[
\text{Na}_2\text{S}
\]

I. 

\[
2 \text{Na} + \text{S} = \text{Na}_2\text{S}
\]

45.99 32.07 78.06

The reaction is carried out in liquid ammonia using the apparatus of Fig. 159.
A weighed tube containing very pure, vacuum distilled Na (see section on Alkali Metals) is opened by breaking off the tip and is quickly pushed into the side arm $A$ of the apparatus. The latter is immediately capped off. After evacuating through $B$, $A$ is carefully heated until the metal melts and flows through the capillary $k$ onto the frit plate $F$. The small amount of oxide that formed when the tip was broken off remains in the ampoule. A vigorous stream of dry, carefully purified $N_2$ is then introduced through $E$, $A$ is opened again, the empty ampoule is removed, and the weight of reactant Na is determined by reweighing the ampoule. The quantity of sulfur required for the reaction is introduced at $O$. Vessel $R$ is cooled with a Dry Ice bath, and about 100 ml. of pure $NH_3$ is condensed on top of the sulfur. The frit plate $F$ and the sharply bent part of tube $u$ are then cooled until some $NH_3$ collects above the frit; a portion of the Na dissolves in this. The ammonia vapor then produces a higher pressure in the space above $F$ than in $R$, and this ammoniacal Na solution is forced into $R$ where it contacts the ammoniacal $S$ solution. This procedure is repeated until all the Na has been extracted from the frit with small portions of $NH_3$. At first, sodium polysulfides are formed in $R$ because of the excess $S$; these gradually degrade to $Na_2S$ as more Na solution is added. By gradually removing the cooling bath at $P$, the $NH_3$ is then allowed to evaporate slowly over a period of several hours. Toward the end of this period, a white precipitate separates. The last traces of $NH_3$ must be evaporated particularly carefully to prevent spattering of the crystals. Finally, the apparatus is evacuated for some time with an oil pump and vessel $R$ is heated for 0.5 hour at 400-500°C. The crystals are pulverized by vigorous shaking and are forced into storage tubes $K$ by tipping the apparatus. The tubes are sealed off in vacuum or $N_2$ atmosphere. The $Na_2S$ is very pure; the yield is almost quantitative.
II. \[ \text{Na}_2\text{S} \cdot 9\text{H}_2\text{O} = \text{Na}_2\text{S} + 9\text{H}_2\text{O} \]

240.21 78.06 162.15

Pure \( \text{Na}_2\text{S} \cdot 9\text{H}_2\text{O} \) is allowed to stand for 14 days in vacuum over concentrated sulfuric or phosphoric acid. The temperature should be 15°C at the start, later 30 to 35°C. The resulting salt contains only 4% \( \text{H}_2\text{O} \). The last traces of water are removed by heating the material to 700°C in a glass or porcelain tube in a fast stream of dry, well-purified \( \text{H}_2 \). Granular, pure white \( \text{Na}_2\text{S} \) of 99.5–99.8% purity is obtained.

**PROPERTIES:**

White crystals; very hygroscopic; discolors rapidly in moist air. M.p. 1180 ± 10°C (in vacuum); d 1.86.

Readily soluble in water; solutions have a strongly alkaline reaction.

Crystallizes in C1 structure type.

**REFERENCES:**


---

**Potassium Sulfide**

\( \text{K}_2\text{S} \)

2\( \text{K} \) + \( \text{S} \) = \( \text{K}_2\text{S} \)

78.19 32.07 110.26

The preparation is carried out in liquid \( \text{NH}_3 \) in the apparatus shown in Fig. 160.

A weighed tube containing very pure, vacuum-distilled potassium (see section on Alkali Metals) is opened by breaking off the tip and is quickly pushed into side arm \( \mathcal{A} \); the latter is immediately capped off. The system is then evacuated through \( \mathcal{B} \) with a high-vacuum pump, and \( \mathcal{A} \) is heated carefully until the metal melts and flows through the capillary \( \kappa \) into the reaction vessel \( \mathcal{R} \). Small amounts of oxide which formed on opening the ampoule remain in the latter. After a vigorous stream of dry, carefully purified \( \text{N}_2 \) is introduced at \( \mathcal{B} \), \( \mathcal{A} \) is reopened and the exact weight of reactant metal is determined by removing and reweighing the ampoule. The stoichiometric quantity of sulfur is then introduced at \( \mathcal{C} \), while the passage of \( \text{N}_2 \) is continued. Vessel \( \mathcal{R} \) is then cooled with a Dry Ice
bath, and 100 ml. of pure NH₃ is condensed on top of both reactants. The reaction forming K₂S is quantitative if the NH₃ is then allowed to reevaporate over a period of several hours through drying tubes filled with KOH. The ammoniacal solution becomes colorless toward the end, and the K₂S separates as a white precipitate. As the last traces of NH₃ are removed, the evaporation is slowed down by frequent cooling in order to prevent spattering of the crystals in the reaction vessel. At the end of the run, the system is evacuated for some time with the oil pump and vessel R is heated for 0.5 hour at 400-500°C. The crystals are pulverized by shaking and transferred into storage tubes K by tipping the apparatus. The tubes are then sealed off in vacuum or in a N₂ atmosphere. The K₂S is very pure; the yield is almost quantitative.

The procedure given above for Na₂S may also be used for K₂S.

Fig. 160. Preparation of potassium sulfide.

**PROPERTIES:**

White crystalline powder; very hygroscopic and sensitive to air. M.p. 912°C; d 1.74.

Readily soluble in water; solutions give a strongly alkaline reaction.

Crystallizes in C 1 structure type.

**REFERENCES:**


See also J. Goubeau, H. Kolb and H. G. Krall, Z. anorg. allg. Chem. 236, 45 (1938).

### Sodium Disulfide

**Na₂S₂**

1. 

\[
\text{Na₂S₄} + 2 \text{Na} = 2 \text{Na₂S₂}
\]

| 174.25 | 45.99 | 220.24 |

A solution of Na₂S₄ in absolute alcohol is prepared according to the directions given on p. 365. While the solution is kept warm
and a continuous stream of \( H_2 \) or \( N_2 \) is passed through, 4 g. of shiny Na, cut into fairly large pieces, is introduced rapidly one after another, by briefly removing the reflux condenser. The solution is then heated for about 30 minutes at 80°C. The light yellow \( \text{Na}_2\text{S}_2 \) precipitate is rapidly suction-filtered through a glass frit in a vigorous \( H_2 \) or \( N_2 \) stream. It is thoroughly washed several times with absolute alcohol in order to remove occluded \( \text{Na}_2\text{S}_4 \) and adhering mother liquor. It is then allowed to stand in a vacuum desiccator over \( P_2\text{O}_5 \). Even after a fairly long time in the desiccator, the product still contains about 4% of tenaciously adhering \( \text{C}_2\text{H}_5\text{OH} \). The yield is 7-8 g. of \( \text{Na}_2\text{S}_2 \).

\[
\begin{align*}
\text{II.} & \quad \text{Na}_2\text{S} + S = \text{Na}_2\text{S}_2 \\
& \begin{array}{c}
78.06 \\
32.07 \\
110.13
\end{array}
\end{align*}
\]

About 2.5 g. of \( \text{Na}_2\text{S} \) and the stoichiometric quantity of \( S \) are placed in a Pyrex tube in a vigorous stream of dry, \( O_2 \)-free \( N_2 \). After the tube has been sealed off in high vacuum, the reactants are fused at 500°C in an electric furnace until completely homogenized (about 45 minutes are required). The melt solidifies on cooling to form yellow, very hard \( \text{Na}_2\text{S}_2 \).

\[
\begin{align*}
\text{III.} & \quad 2\text{Na} + 2S = \text{Na}_2\text{S}_2 \\
& \begin{array}{c}
45.99 \\
64.13 \\
110.12
\end{array}
\end{align*}
\]

This method of preparation from the elements (in liquid \( \text{NH}_3 \)) given by Fehér and Berthold, follows in principle the method worked out by Klemm and co-workers for preparing \( \text{Na}_2\text{S} \) (method I, p. 358).

SYNONYM:

Disodium disulfane.

PROPERTIES:

Light yellow, microcrystalline, very hygroscopic powder. Gradually darkens on heating and at 400°C is a light reddish-brown. Above 475°C, the color deepens to dark brown and the substance sinters, M.p. \( \sim 490°C \). The deep brown melt is very mobile. After solidification and thorough grinding in a mortar, only the preparation obtained from liquid ammonia retains the original yellow color. The products prepared from alcohol are always olive green after melting. X-ray studies have shown that sodium disulfide occurs in two modifications, a low-temperature modification
(α-Na₂S₂) and a high-temperature modification (β-Na₂S₂). The lines of pure α-Na₂S₂ were observed only in preparations isolated from alcoholic solution. Products which solidified from a melt or were exposed to higher temperatures have the lattice of the β-modification. Irreversible transition from one modification to the other occurs between 150 and 250°C.

REFERENCES:


**Potassium Disulfide**

\[ K_2S_2 \]

I. \[ K_2S + S = K_2S_2 \]

The procedure is the same as in method II for Na₂S₂. On cooling the melt, a hard yellow cake of K₂S₂ is formed.

II. \[ 2K + 2S = K_2S_2 \]

Prepared in liquid NH₃ analogously to method III for Na₂S₂.

SYNONYM:

Dipotassium disulfane.

PROPERTIES:

From liquid NH₃, it is a fine, pale yellow powder which, after heating at 150°C in vacuum for several hours, is free of all NH₃. Extremely hygroscopic and sensitive to air. The aqueous solution is light yellow. On heating in vacuum, K₂S₂ gradually darkens and at 440°C is deep orange. At higher temperatures, the substance sinters; at 500°C it is a dark red-violet and it melts at about 520°C to form a dark brown fluid. After pulverizing, the solidified melt
reverts to the original yellow color. d (20°C) 1.973. Occurs in only one modification.

REFERENCES:

I. The same as for Na₂S₂ (II).
II. The same as for Na₂S₂ (III); F. Fehér and H. J. Berthold, Z. anorg. allg. Chem. 274, 223 (1953).

**Potassium Trisulfide**

K₂S₃

I. 

\[ \text{K}_2\text{S} + 2\text{S} = \text{K}_2\text{S}_3 \]

110.26 64.13 174.39

The reaction is carried out in absolute alcohol. A solution of 5.0 g. of shiny K in 72 ml. of carefully dehydrated ethanol is prepared in a round-bottom flask equipped with a reflux condenser and a drying tube. After the evolution of H₂ ends, exactly half the solution is decanted and is saturated with H₂S (in the absence of atmospheric moisture) in the manner described for NaHS. Excess H₂S is removed by brief boiling in a stream of N₂ or H₂. The two portions of the solution are then recombined in the original reaction flask. This K₂S solution is then mixed with 4.1 g. of pure S and boiled for 30 minutes; orange-yellow K₂S₃ crystals separate. These are quickly suction-filtered in a fast \( \text{H}_2 \) or \( \text{N}_2 \) stream, washed with absolute ethanol, and freed of adhering solvent in a vacuum desiccator over \( \text{P}_2\text{O}_5 \).

II. The solid starting materials are melted together. The procedure is the same as in method II for Na₂S₂. A brown hard cake of K₂S₃ is formed on cooling the melt.

SYNONYM:

Dipotassium trisulfane.

PROPERTIES:

Well crystallizing, yellow-orange compound, which is readily soluble in water, giving a yellow solution. On heating, the substance becomes increasingly darker, begins to sinter above 284°C, and melts at about 292°C to form a brown-black melt. After solidification and pulverization, K₂S₃ has a greenish-brown color. The preparations made by the melt process are of the same color. d (20°C) 2.102.
REFERENCES:


II. The same as for Na$_2$S$_2$ (II).

Products of the analytical composition Na$_2$S$_3$ may be prepared from the elements either in liquid ammonia or in a melt. However, these products are simply equimolar mixtures of Na$_2$S$_2$ and Na$_2$S$_4$.

REFERENCE:


**Sodium Tetrasulfide**

Na$_2$S$_4$

1. 2NaHS + 3S = Na$_2$S$_4$ + H$_2$S

112.14 96.20 174.25 34.09

A mixture of 50 ml. of absolute alcohol and about 2 g. of fairly small pieces of shiny Na is prepared in a 150-ml. flask equipped with a reflux condenser and an (initially closed) side arm for holding a gas inlet tube. A drying tube on the condenser prevents contact with atmospheric moisture. After all the Na has dissolved to the ethoxide, a glass tube extending to the bottom of the flask is introduced through the side arm. It is sealed tightly in place, and pure, carefully dried H$_2$S is passed through it to saturate the solution. The slight precipitate of NaHS which sometimes forms is not troublesome since it redissolves during the reaction. Then the stoichiometric quantity of pure, very finely powdered S (2.00 g. of Na corresponds to 4.17 g. of S) is added and the reaction mixture boiled for one hour on a steam bath while a vigorous stream of O$_2$-free, dry H$_2$ or N$_2$ is passed through. A dark-red solution of Na$_2$S$_4$ is formed. This is condensed to 5 ml. in vacuum at about 40°C, causing a dense, yellow precipitate of Na$_2$S$_4$ to separate. The product is rinsed out onto a fritted filter with some absolute alcohol, quickly suction-filtered in a vigorous H$_2$ or N$_2$ stream, and washed with some alcohol. On prolonged standing in a vacuum desiccator over P$_2$O$_5$, it loses the adhering alcohol except for small, stubbornly retained quantities (about 2–3%). The yield is 5–6 g.
II. \[ \text{Na}_2\text{S} + 3\text{S} = \text{Na}_2\text{S}_4 \]
\[ \begin{array}{c|c|c}
78.06 & 96.20 & 174.26 \\
\end{array} \]

The procedure is the same as that described in method II for \( \text{Na}_2\text{S}_2 \). A grayish-yellow, hard cake of \( \text{Na}_2\text{S}_4 \) is formed on cooling the melt.

SYNONYM:

Disodium tetrasulfane.

PROPERTIES:

Sodium tetrasulfide formed from alcoholic solution is a hygroscopic, orange-yellow crystalline powder. The aqueous solution is yellow at room temperature and dark red at the boiling point. Becomes brown on heating, begins to sinter at 284°C, melts at 286°C to a brown-black mass. After solidification, the substance is green, \( d \) (20°C) 2.08.

REFERENCES:

The same as for \( \text{Na}_2\text{S}_2 \) (I and II).

**Potassium Tetrasulfide**

\( \text{K}_2\text{S}_4 \)

I. \[ \text{K}_2\text{S} + 3\text{S} = \text{K}_2\text{S}_4 \]
\[ \begin{array}{c|c|c}
110.26 & 96.20 & 206.46 \\
\end{array} \]

The procedure is the same as in method II for \( \text{Na}_2\text{S}_2 \). A hard, wine-red cake of \( \text{K}_2\text{S}_4 \) is formed on cooling the melt.

II. \[ 2\text{K} + 4\text{S} = \text{K}_2\text{S}_4 \]
\[ \begin{array}{c|c|c}
78.19 & 128.26 & 206.45 \\
\end{array} \]

Preparation in liquid \( \text{NH}_3 \) is analogous to that described in method III for \( \text{Na}_2\text{S}_2 \).

SYNONYM:

Dipotassium tetrasulfane.

PROPERTIES:

Orange-yellow solid. The aqueous solution is yellow at room temperature, red at the boiling point. Begins to sinter at 145°C, and melts around 159°C without a sharp melting point. Dark red melt.
On cooling, solidifies to a dark-red, glassy mass. In the preparation of the very pure compound from liquid NH\textsubscript{3}, supercooling of the solution can be eliminated by heating it to 110°C. The color of the substance is then again orange-yellow but slightly more intense than before the melting.

REFERENCES:
The same as for Na\textsubscript{2}S\textsubscript{2} (II) and K\textsubscript{2}S\textsubscript{2} (II).

**Sodium Pentasulfide**

Na\textsubscript{2}S\textsubscript{5}

\[
\text{Na}_2\text{S} + 4\text{S} = \text{Na}_2\text{S}_5
\]

78.06 128.26 206.32

The procedure is the same as in method II for Na\textsubscript{2}S\textsubscript{2}. A hard, grayish-yellow cake of Na\textsubscript{2}S\textsubscript{5} is formed on cooling the melt.

SYNONYM:
Disodium pentasulfane.

PROPERTIES:
Yellowish-brown powder, very hygroscopic. The microscope reveals uniform, light yellow, partly transparent crystal fragments. If dissolved in freshly boiled water or dilute sodium hydroxide, slight precipitation of S takes place. This disappears almost completely when the solution is heated.
M.p. 253°C; d (20°C) 2.08.

REFERENCES:
The same as for Na\textsubscript{2}S\textsubscript{2} (I and II).

**Potassium Pentasulfide**

K\textsubscript{2}S\textsubscript{5}

\[
2\text{KHS} + 4\text{S} = \text{K}_2\text{S}_5 + \text{H}_2\text{S}
\]

144.34 128.26 238.52 34.08

In principle, the reaction is the same as that described in method I for Na\textsubscript{2}S\textsubscript{4}. The experimental procedure is therefore completely analogous.
Dissolving about 2 g. of K in 30 ml. of anhydrous C\textsubscript{2}H\textsubscript{5}OH and subsequent saturation with H\textsubscript{2}S yields an (absolute) alcoholic KHS solution. This solution is then mixed with the stoichiometric quantity of very finely powdered S (2.00 g. of K corresponds to 3.28 g. of S) and is then boiled for one hour on a steam bath while H\textsubscript{2} or N\textsubscript{2} is passed through. The reaction is instantaneous and is accompanied by H\textsubscript{2}S evolution and discoloration of the solution; after a short time, a light orange-red precipitate of K\textsubscript{2}S\textsubscript{5} is formed. The quantity of this precipitate increases considerably if the solution is then concentrated in vacuum to about 5 ml. The K\textsubscript{2}S\textsubscript{5} is then quickly suction-filtered in a vigorous H\textsubscript{2} or N\textsubscript{2} stream, washed with some absolute ethanol, and freed of adhering solvent in a vacuum desiccator over P\textsubscript{2}O\textsubscript{5}. The yield is about 5 g.

\[
\text{II.} \quad \text{K}_2\text{S} + 4\text{S} = \text{K}_2\text{S}_5
\]

The procedure is the same as described in method II for Na\textsubscript{2}S\textsubscript{2}. A hard, dark-brown cake of K\textsubscript{2}S\textsubscript{5} is formed on cooling the melt.

SYNONYM:

Dipotassium pentasulfane.

PROPERTIES:

Depending on the method of preparation, orange-red, shiny crystals or dark brown, microcrystalline mass. After a short exposure to air the crystals become coated with a sulfur layer. A solution in CO\textsubscript{2}-free water is yellow to orange-red and becomes deep, dark red at the boiling point. On heating in vacuum, the substance at first becomes dark red and then, at 190°C, deep violet. M.p. 211°C; d (20°C) 2.128.

REFERENCES:

The same as for Na\textsubscript{2}S\textsubscript{2} (I and II) and K\textsubscript{2}S\textsubscript{2} (II).

Potassium Hexasulfide

K\textsubscript{3}S\textsubscript{6}

About 5 g. of K\textsubscript{2}S\textsubscript{5} is heated together with the required quantity of S for several hours in an evacuated glass tube. The temperature is between 220°C and 280°C, and heating is continued until a completely homogeneous melt is obtained. This procedure is analogous
to that described in method II for Na₃S₂. The melt is allowed to cool slowly over a period of about 10 hours.

SYNONYM:

Dipotassium hexasulfane.

PROPERTIES:

After pulverizing, K₃S₆ has a red to reddish-brown color and no longer forms a clear solution in water. Sintering starts at about 184°C. M.p. 196°C; d (20°C) 2.02.

REFERENCES:

The same as for K₃S₂ (II).

The other alkali metal sulfides Rb₃S₂, Rb₂S₃, Rb₂S₅, Cs₂S₂, Cs₂S₃ and Cs₂S₅ can be prepared from the elements in liquid NH₃ in the same way as described in method III for Na₂S₂.

REFERENCE:


**Ammonium Pentasulfide**

\[(\text{NH}_4)_2\text{S}_5\]

\[
2 \text{NH}_3 + \text{H}_2\text{S} + 4 \text{S} = (\text{NH}_4)_2\text{S}_5
\]

A mixture of 80 g. of finely crystalline S in 200 ml. of concentrated ammonium hydroxide (d 0.88, about 35%) is prepared in a one-liter round-bottom flask with a side gas inlet tube reaching to the bottom of the flask. After the closed flask has been weighed, a moderately fast stream of pure, dry H₂S is passed through the suspension. The neck of the flask carries a one-hole rubber stopper closed off with a plug of absorbent cotton. This flow impediment causes a constant positive pressure within the vessel and thus prevents the inflow of atmospheric O₂. The solution is at first orange and later becomes dark red; the S dissolves, with occasional shaking, after 60 to 80 minutes. More H₂S is then introduced until a total of about 35 g. is absorbed. The impurities are then removed by rapid suction-filtering of the dark
solution. The filtrate is allowed to stand in a tightly sealed flask at room temperature or on ice until crystallization occurs. After several hours, yellow needles of \((\text{NH}_4)_2\text{S}_5\) are formed. These are stable for a fairly long time if submerged in the mother liquor in the absence of air, but they decompose very rapidly when dry to form \(\text{NH}_3\), \(\text{H}_2\text{S}\) and \(\text{S}\). The product is isolated by rapid suction-filtration through filter paper, removal of adhering mother liquor by pressing between filter papers, and consecutive washing with ether-methanol (5:1), absolute ether and anhydrous chloroform. The still moist product is allowed to stand in a vacuum desiccator over CaO which has been wetted with some concentrated ammonium hydroxide. However, because of decomposition, it contains about 10% of elemental sulfur after five hours. Freshly prepared \((\text{NH}_4)_2\text{S}_5\) should give a clear solution in 5% ammonium hydroxide.

SYNONYM:

Diammonium pentasulfane.

PROPERTIES:

Yellow to orange-yellow crystals; very easily decomposed to \(\text{NH}_3\), \(\text{H}_2\text{S}\) and \(\text{S}\). Melts in a sealed tube at 95°C to form a red liquid; decomposes on heating in an open tube. Rapidly precipitates \(\text{S}\) with water; soluble in ammonium hydroxide (see above).

REFERENCE:


**Dichloromonosulfane**

\[ \text{S} + \text{Cl}_2 = \text{S}\text{Cl}_2 \]

32.07 70.91 102.98

Coarsely ground roll sulfur (200 g.) is placed in a one-liter, round-bottom, ground glass flask equipped with a side arm serving as gas inlet. A reflux condenser is set in the ground joint and a thermometer is fastened in such a way that it protrudes from the flask into the lower part of the condenser. From the upper end of the condenser an outlet tube leads to the hood through a wash bottle containing \(\text{H}_2\text{SO}_4\). A fast stream of carefully dried \(\text{Cl}_2\) gas is passed through the S until the contents of the flask have completely liquefied, forming crude \(\text{S}_2\text{Cl}_2\) (heat is evolved). Then a
7. **SULFUR, SELENIUM, TELLURIUM**

spatula tip (about 0.1 g.) of Fe powder or anhydrous FeCl$_2$ or FeCl$_3$ is added and the gas flow is continued for another 0.5 hour; during this time the reaction mixture is gradually cooled to 20°C by immersing the flask in water. The dark red liquid which forms, and which contains S$_2$Cl$_2$ and Cl$_2$ in addition to the SC1$_2$, is left to stand for about one hour. Then 2 ml. of PCl$_3$ is added and the solution is distilled through a small fractionating column. The middle fraction boiling between 55 and 62°C is collected in a receiver containing a few drops of PCl$_3$ and is again fractionated. A very pure product with a constant boiling point of 60°C is obtained. The yield is about 70%.

The substance is stable for a few days when stored in glass vessels in the presence of a few drops of PCl$_3$. Pure SCl$_2$ can always be recovered from the mixtures with S$_2$Cl$_2$ and Cl$_2$ that form on prolonged standing by distillation with PCl$_3$.

II. \[
S_2Cl_2 + Cl_2 = 2SCl_2
\]

The substance can also be prepared starting directly with S$_2$Cl$_2$. Otherwise, the procedure is the same as in method I.

**SYNONYM:**

Sulfur dichloride.

**PROPERTIES:**

Dark-red liquid with a pungent, chlorinelike odor; it decomposes readily, reversing reaction II, to form S$_2$Cl$_2$ and Cl$_2$; sensitive to atmospheric moisture. M.p. -121°C, b.p. +59.6°C; \( \rho \) (20°C) 1.621. Reacts with water with precipitation of sulfur and formation of H$_2$SO$_3$, H$_2$SnO$_6$ and H$_2$SO$_4$; soluble in n-hexane without decomposition.

**REFERENCES:**

See also Naturforschung und Medizin in Deutschland 1939-1946 (FIAT-Review), 23, 191.

**Dichlorodisulfane**

\[
S_2Cl_2
\]

64.13 70.91 135.04

Sulfur is melted in a flask equipped with a side arm and a neck elongated into a gradually narrowing tube. By tilting the flask, the
walls are coated with a uniform layer of sulfur melt. After cooling, the flask is mounted vertically in such a way that the tube end passes through a rubber stopper into another flask below. From the latter, a gas outlet tube passes through a drying tube directly to the hood. A moderately rapid stream of carefully dried Cl₂ is introduced through the side arm of the top flask and the walls of that flask are simultaneously heated to 50-80°C by fanning with a flame. Once the reaction is in progress, the S₂Cl₂ product flows into the lower flask in a rapid succession of drops. The orange-red substance is still contaminated by dissolved starting materials. Some sulfur is added and it is distilled at atmospheric pressure. The portion which distills above 137°C is fractionated over sulfur at about 12 mm. in an apparatus with ground glass joints; b.p. of the pure product is 29-30°C at this pressure.

This material is used on a large scale in industry as a solvent for sulfur in the vulcanization of rubber.

SYNONYMS:

Disulfur dichloride; older designations "sulfurous chloride" and "sulfur monochloride."

PROPERTIES:

Golden yellow, oily liquid; when less pure, orange to reddish because of SCl₂ impurities; fumes in moist air, unpleasant pungent odor. M.p. -77°C, b.p. (760 mm.) +138°C; d (20°C) 1.6773.

Hydrolyzes with water to form HCl, SO₃ and H₂S; these then convert to S, H₂S₂O₃ and H₂S₃O₆. Readily soluble in CS₂.

REFERENCE:


**Dichlorotri-, -tetra-, -penta-, -hexa-, -hepta- and -octasulfane**

S₂Cl₂, S₃Cl₂, S₄Cl₂, S₅Cl₂, S₆Cl₂, S₇Cl₂, S₈Cl₂

If the ratios of the reactants are reversed, then the general synthetic method used in the preparation of the sulfanes (p. 353) can also be used for the preparation of the chlorosulfanes. The sulfane component is added to an excess of chlorosulfane at low temperature and after the reaction

\[(a - 2) \text{Cl}_2\text{S}_n + \text{Cl} - \text{S}_n - \frac{\text{Cl} + \text{H}}{\text{H} + \text{Cl}} - \text{S}_m - \frac{\text{Cl}}{} - \text{Cl} = \text{Cl}_2\text{S}_{2n+m} + 2 \text{HCl} + (a - 2) \text{Cl}_2\text{S}_n\]

\[(n = 1, 2; m = 1, 2, 3, 4, 5, 6).\]

is complete, excess chlorosulfane \((a - 2)\text{Cl}_2\text{S}_n\) is distilled off.

With suitable choice of reactants and careful following of
analogous preparative conditions, it is possible to obtain pure \(S_3\text{Cl}_2\), \(S_4\text{Cl}_2\), \(S_5\text{Cl}_2\), \(S_6\text{Cl}_2\), \(S_7\text{Cl}_2\) and \(S_8\text{Cl}_2\).

In general, the chlorosulfanes are best made from the following components:

<table>
<thead>
<tr>
<th>Desired chlorosulfane</th>
<th>Chlorosulfane component</th>
<th>Sulfane component</th>
</tr>
</thead>
<tbody>
<tr>
<td>(S_3\text{Cl}_2)</td>
<td>(\text{SCl}_2)</td>
<td>(\text{H}_2\text{S})</td>
</tr>
<tr>
<td>(S_4\text{Cl}_2)</td>
<td>(\text{SCl}_2)</td>
<td>(\text{H}_2\text{S}_2)</td>
</tr>
<tr>
<td>(S_5\text{Cl}_2)</td>
<td>(\text{S}_2\text{Cl}_2)</td>
<td>(\text{H}_2\text{S})</td>
</tr>
<tr>
<td>or (\text{SCl}_2)</td>
<td></td>
<td>(\text{H}_2\text{S}_3)</td>
</tr>
<tr>
<td>(S_6\text{Cl}_2)</td>
<td>(\text{S}_2\text{Cl}_2)</td>
<td>(\text{H}_2\text{S}_2)</td>
</tr>
<tr>
<td>or (\text{SCl}_2)</td>
<td></td>
<td>(\text{H}_2\text{S}_4)</td>
</tr>
<tr>
<td>(S_7\text{Cl}_2)</td>
<td>(\text{S}_2\text{Cl}_2)</td>
<td>(\text{H}_2\text{S}_3)</td>
</tr>
<tr>
<td>(S_8\text{Cl}_2)</td>
<td>(\text{S}_2\text{Cl}_2)</td>
<td>(\text{H}_2\text{S}_4)</td>
</tr>
</tbody>
</table>

The same rules as those for the preparation of sulfanes (p. 349) apply for these procedures, particularly as far as cleaning the glass equipment is concerned.

The syntheses of \(S_3\text{Cl}_2\) and \(S_4\text{Cl}_2\) are described as examples.

**Dichlorotrisulfane**

\[ \text{S}_3\text{Cl}_2 \]

\[
\begin{array}{cccc}
\text{Cl} & \text{--S--} & \frac{\text{Cl} + \text{H}}{\text{--S--}} & \frac{\text{H} + \text{Cl}}{\text{S--Cl}} = \text{S}_3\text{Cl}_2 + 2\text{HCl} \\
102.98 & 34.08 & 102.98 & 167.11 72.93
\end{array}
\]

**Excess SCl₂**

The two-liter, three-neck flask \(a\) of Fig. 161, equipped with a Hg-seal stirrer, is charged with 2400 g. of freshly distilled SCl₂ and is cooled with stirring to \(-80^\circ\text{C}\) in a large Dewar flask filled with Dry Ice-methanol mixture; the flask must be completely immersed in the cooling bath. The CaCl₂ tube \(b\) prevents penetration of atmospheric moisture. About 45 ml. of previously condensed H₂S (compare preparation of tetrasulfane, p. 353) is combined with the SCl₂ at about \(-80^\circ\text{C}\) by attaching the trap filled with liquid H₂S directly to the somewhat inclined ground glass joint \(c\) and emptying it by slow rotation of the male ground glass joint. The reaction, barely visible from the outside, is complete in 12-14 hours; the
cooling bath is then removed and the solution allowed to warm slowly to about 0°C with constant stirring.

After most of the dissolved HCl has escaped, an accurately fitting riser tube is placed on the middle ground glass joint d, as shown in Fig. 161. This tube is connected to the side arm of distillation flask e by means of a short piece of rubber tubing. Flask e is then evacuated with an aspirator. The input of the reaction mixture to e is regulated by means of stopcock f. The distillation flask is heated with a small burner and dry, purified N₂ is introduced through the capillary g to aid the boiling. The 500-ml. trap h, cooled with a Dry Ice-methanol bath, can be emptied from time to time into flask i through the sealed-in siphon by briefly releasing the aspirator vacuum. After the bulk of the solvent is removed — two hours are needed to distill off two liters of SCl₂ — the product is transferred into the two-neck flask of the high-vacuum apparatus.
shown in Fig. 162. Here the remaining solvent is removed and collected in the liquid-nitrogen-cooled trap at the pump (not shown in the diagram). Only then is \( J_1 \) cooled with an ice-water bath and \( J_2 \) with a Dry Ice-methanol bath. The flask is then heated on a water bath of 40-50°C; the \( S_3Cl_2 \) slowly distills and mostly condenses in \( J_1 \) (b.p. 30.5°C at 10^-4 mm.).

In this manner, about 100 g. of \( S_3Cl_2 \) may be distilled in five hours. The yield of pure \( S_3Cl_2 \) is 50%.

A simplified procedure for the continuous preparation of larger quantities of dichlorotrisulfane was developed by S. Fehér and J. Goebell.

**Dichlorotetrasulfane**

\[
\text{Cl} - \text{S} \quad [\text{Cl} + \text{H}] \quad \text{S}_2 \quad [\text{H} + \text{Cl}] \quad \text{S} - \text{Cl} = \text{S}_4\text{Cl}_2 + 2\text{HCl}
\]

Excess \( \text{SCL}_2 \)

The apparatus is the same as that for the preparation of dichlorotrisulfane; only the manner of adding the sulfane component is different.

The three-neck flask \( a \), cooled to -80°C with Dry Ice-methanol mixture, contains 1200 g. of freshly distilled \( \text{SCL}_2 \). A separatory funnel, whose tube is drawn into a capillary, is inserted into the ground joint \( c \). About 26 g. of \( \text{H}_2\text{S}_3 \) is added slowly in drops from this funnel over a period of one to two hours. Good agitation of the flask contents must be provided. The reaction is complete in about three hours.

The rest of the procedure is analogous to that for the preparation of \( S_3\text{Cl}_2 \). The residue, a clear, orange-red liquid, is freed of traces of \( \text{SCL}_2 \) in a smaller flask by short standing in high vacuum; it is then nearly pure so that, in contrast to \( S_3\text{Cl}_2 \), distillation is not necessary. The yield is 90%.

The distillation, which involves experimental difficulties, is unnecessary even in the case of higher chlorosulfanes. However, preparations of dichloropenta- and dichlorohexasulfane require about 12 hours for completion, using 25 g. of \( \text{H}_2\text{S}_3 \) and 40 g. of \( \text{H}_2\text{S}_4 \), respectively.

Reaction of about 450 g. of \( S_2\text{Cl}_2 \) with approximately 10 g. of \( \text{H}_2\text{S} \) (10 g. of \( \text{H}_2\text{S}_2 \), \( \text{H}_2\text{S}_3 \) or \( \text{H}_2\text{S}_4 \)) produces \( S_6\text{Cl}_2 \) (\( S_6\text{Cl}_2 \), \( S_7\text{Cl}_2 \), \( S_8\text{Cl}_2 \)). The course of the reaction and the reaction rates are similar to the case in which \( \text{SCL}_2 \) is used.
PROPERTIES:

Starting with $S_2Cl_2$, the higher chlorosulfanes are orange-red, oily liquids with high refractive indexes. They have the same odor as $S_2Cl_2$ but the intensity of their odor decreases rapidly with increasing molecular weight.

<table>
<thead>
<tr>
<th>Formula weight</th>
<th>d (20°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_3Cl_2$</td>
<td>167.09</td>
</tr>
<tr>
<td>$S_4Cl_2$</td>
<td>199.15</td>
</tr>
<tr>
<td>$S_5Cl_2$</td>
<td>231.21</td>
</tr>
<tr>
<td>$S_6Cl_2$</td>
<td>263.27</td>
</tr>
<tr>
<td>$S_7Cl_2$</td>
<td>295.33</td>
</tr>
<tr>
<td>$S_8Cl_2$</td>
<td>327.39</td>
</tr>
</tbody>
</table>

In this homologous series, the density of the last two members can only be obtained by extrapolation because of their increased viscosity and decreased purity compared to the first members.

REFERENCES:


Sulfur Tetrachloride

$SCl_4$

$SCl_2 + Cl_2 = SCl_4$

102.98 70.91 173.89

Leg $A$ of the apparatus shown in Fig. 163 is filled to about one third with pure $SCl_2$ and then sealed off at $C$. The stoichiometric quantity of $Cl_2$ is then condensed in the graduated tube $B$, cooled with a Dry Ice bath. The tube is then sealed off at $D$. Leg $A$ is then also cooled to $-78^\circ$C and the apparatus is tilted so that the $SCl_2$ flows quickly into the $Cl_2$ in $B$. The mixture is vigorously shaken. It solidifies immediately, forming white (occasionally pale yellow) $SCl_4$.

The product can be stored only in sealed tubes at low temperatures.

The analogous preparation from $S_2Cl_2$ and liquid $Cl_2$ is not recommended since the formation of the intermediate $SCl_2$ proceeds very slowly in the absence of a catalyst, and the reaction therefore takes several days.
7. SULFUR, SELENIUM, TELLURIUM

Fig. 163. Preparation of sulfur tetrachloride.

PROPERTIES:

Fine white powder; stable only as a solid at low temperatures; decomposes above $-30^\circ$C into \( \text{SCl}_2 \) and \( \text{Cl}_2 \); sensitive to moisture. Solid \( \text{SCl}_4 \) sinters at $-30^\circ$C and melts between $-30$ and $-20^\circ$C with simultaneous decomposition.

Hydrolyzed by water to \( \text{HCl} \) and \( \text{SO}_2 \).

REFERENCES:

See also O. Ruff, Ber. dtsch. chem. Ges. 37, 4513 (1904).

Dibromodisulfane

\[
\text{S}_2\text{Br}_2
\]

I. \[
2 \text{S} + \text{Br}_2 = \text{S}_2\text{Br}_2
\]

64.13 159.83 223.96

The procedure is based on that described by Ruff and Winterfield. Thus, 94 ml. of \( \text{Br}_2 \) is slowly added to 119 g. of \( \text{S} \) (recrystallized from \( \text{CS}_2 \)) in a dry 500-ml. pressure flask capable of withstanding 20 atm. of internal pressure. (If proper precautions are observed, a beer bottle can be used.) The mixture is heated for two hours on a steam bath. The dark-red liquid product is distilled at 0.1 mm. The first cut contains primarily unreacted \( \text{Br}_2 \); the main fraction distilling between 46 and 48°C is pure \( \text{S}_2\text{Br}_2 \), while crystalline \( \text{S} \) remains in the distillation flask.

The yield averages 80%.
The reaction is carried out in the apparatus shown in Fig. 164. Hydrogen bromide is produced by allowing Br₂ to drip into tetralin (see p. 282 for this procedure); to remove traces of elemental bromine, the HBr is passed through a wash bottle containing tetralin, through a U tube containing clay fragments and moist red P, and finally through two CaCl₂ drying tubes. This prepurified gas is then bubbled at room temperature through about 30 g. of dichlorodisulfate (see p. 371), contained in a 250-ml. two-neck flask, in such a way that the contents are well mixed. The course of the slightly exothermic reaction can be followed through the gradual coloration of the oil to a dark red. The reaction is complete after 1-2 hours, as confirmed by qualitative testing of the product for chlorine. During the reaction, the excess HBr and the HCl produced are discharged to the hood via a CaCl₂ tube.

SYNONYM:

Disulfur dibromide. Older names “sulfur monobromide” and “sulfurous bromide.”

PROPERTIES:

Dark red, oily liquid which does not wet glass. M.p. -46°C; dissociates on heating into the elements and therefore can be distilled without decomposition only in high vacuum. d.(20°C) 2.629. In H₂O, hydrolyzes to HBr, SO₂ and S. Soluble in CS₂, CCl₄ and C₆H₆.

REFERENCES:


Dibromoti-, -tetra-, -tenta-, -hexa-, -hepta- and -octasulfane

\[ S_3\text{Br}_2, S_4\text{Br}_2, S_5\text{Br}_2, S_6\text{Br}_2, S_7\text{Br}_2, S_8\text{Br}_2 \]

\[
\begin{align*}
S_6\text{Cl}_2 + 2\text{HBr} & \rightarrow S_3\text{Br}_2 + 2\text{HCl} \\
167.11 & \quad 161.85 & \quad 256.03 & \quad 72.93 \\
S_7\text{Cl}_2 + 2\text{HBr} & \rightarrow S_4\text{Br}_2 + 2\text{HCl} \\
199.18 & \quad 161.85 & \quad 288.10 & \quad 72.93 \\
S_8\text{Cl}_2 + 2\text{HBr} & \rightarrow S_5\text{Br}_2 + 2\text{HCl} \\
231.24 & \quad 161.85 & \quad 320.16 & \quad 72.93 \\
S_9\text{Cl}_2 + 2\text{HBr} & \rightarrow S_6\text{Br}_2 + 2\text{HCl} \\
263.31 & \quad 161.85 & \quad 352.23 & \quad 72.93 \\
S_10\text{Cl}_2 + 2\text{HBr} & \rightarrow S_7\text{Br}_2 + 2\text{HCl} \\
295.38 & \quad 161.85 & \quad 384.29 & \quad 72.93 \\
S_11\text{Cl}_2 + 2\text{HBr} & \rightarrow S_8\text{Br}_2 + 2\text{HCl} \\
327.44 & \quad 161.85 & \quad 416.36 & \quad 72.93
\end{align*}
\]

These bromosulfanes are prepared in a manner analogous to \( S_8\text{Br}_2 \) (method II), using the same apparatus. About 30 g. of chlorosulfane is used.

PROPERTIES:

The color of the bromosulfanes lightens with increasing chain length: \( S_2\text{Br}_2 \) is dark red, \( S_4\text{Br}_2 \) only raspberry red. All bromosulfanes are completely miscible with \( CS_2 \). Only the oils containing less sulfur than \( S_4\text{Br}_2 \) are soluble in benzene, toluene and carbon tetrachloride.

\[ d (20^\circ C) \]

\[
\begin{align*}
S_2\text{Br}_2 & \quad 2.52 \\
S_4\text{Br}_2 & \quad 2.47 \\
S_6\text{Br}_2 & \quad 2.41 \\
S_8\text{Br}_2 & \quad 2.36 \\
S_7\text{Br}_2 & \quad 2.33 \\
S_8\text{Br}_2 & \quad 2.30
\end{align*}
\]

REFERENCES:

See \( S_2\text{Br}_2 \) (II).

Lower Sulfur Oxides

\( S_2\text{O}, \text{SO} \)

See the original literature for the preparation of these compounds.
REFERENCES:


Disulfur Trioxide

\[ S + SO_3 = S_2O_3 \]

32.07 80.07 112.14

The Pyrex apparatus (Fig. 165) consists of distillation flasks A, B and C (300 ml. each), reaction vessel D, and U tube K, filled with a \( P_2O_5 \)-glass wool mixture. To start the run, about 1 g. of carefully purified S (see p. 341) is charged into vessel D through ground glass joint J, and 200 ml. of pure, 65% oleum is placed in the flask A. Then A is heated very slowly in an \( H_2SO_4 \) bath while B is cooled in an ice-water bath and C with an ice-salt bath. Most of the \( SO_3 \) condenses in B and only a small amount passes into C. As soon as all the \( SO_3 \) which can be removed from the acid by gentle heating is evaporated, flask A is allowed to cool and is then

Fig. 165. Preparation of disulfur trioxide.
disconnected at joint $E$; the latter is immediately closed off. About three quarters of the $SO_3$ in $B$ is then distilled into $C$ in the same manner by cooling $C$ with ice water and $D$ with an ice-salt mixture. Flask $B$ is then disconnected at $F$. If the product collected in $C$ is not yet sufficiently pure (it should melt at 15-16°C to a colorless liquid), it must be redistilled using flasks $A$ and $B$ (which are meanwhile cleaned and dried). To achieve the reaction, the $SO_3$ in $C$ is heated until it melts, and 15 ml. of the melt is allowed to deposit on the sulfur in $D$ by rotating the flask in the ground glass joint $G$. The mixture instantaneously turns a deep blue. A vigorous reaction starts after 30 seconds, evolving white vapors. It is then advisable to disconnect the $P_2O_5$ tube at $H$ from time to time. It is important to maintain the flask contents at approximately 15°C at all times. Above that temperature, the product $S_2O_3$ is markedly decomposed, while at lower temperatures the excess $SO_3$ solidifies. If this happens, separation of the $SO_3$ becomes very difficult and is accompanied by partial decomposition of the $S_2O_3$.

The reaction subsides after about two minutes. The mixture is then thoroughly shaken and allowed to stand for five minutes. The solid bluish-green $S_2O_3$ settles to the bottom and the almost colorless $SO_3$ above it can be poured back into flask $C$ by careful tipping. Adhering traces of $SO_3$ are removed by subsequent warming in a vigorous $CO_2$ stream. The initial temperature for this operation is 50°C, which later is reduced to 40°C. When almost all the $SO_3$ is removed; the contents are rapidly poured into a second dry vessel of the same type and $CO_2$ is again introduced; the ground glass cap is lifted from time to time and the crystal mass carefully crushed with a glass rod. The surface of the otherwise blue substance begins to turn brown after quantitative removal of the $SO_3$. Carbon dioxide is then passed over the product for a further 20 minutes. The temperature should not exceed +10°C. Following this operation, the product has the theoretical composition. The yield is about 3 g.

Disulfur trioxide must be stored below +15°C in a dry, oxygen-free atmosphere at pressures below 1 mm., but even under these conditions it is stable for only a few hours.

PROPERTIES:

Blue-green, crystalline substance; extremely hygroscopic; decomposes readily, particularly above +15°C, into $SO_2$, $SO_3$ and S. Reacts with water with fizzing to form $S$, $H_2SO_4$ and $H_3SnO_3$.

Soluble in oleum, giving a deep blue or brown color, depending on the $SO_3$ content of the acid; insoluble in pure $SO_3$.

REFERENCES:


**Polysulfur Peroxide**

\[(\text{SO}_3)_x\]

See the original literature for the preparation of this compound.


**Thionyl Chloride**

\[\text{SOCl}_2\]

I. \[\text{SCl}_2 + \text{SO}_3 = \text{SOCl}_2 + \text{SO}_2\]

<table>
<thead>
<tr>
<th></th>
<th>102.98</th>
<th>80.07</th>
<th>118.98</th>
<th>64.07</th>
</tr>
</thead>
</table>

Flask A of the apparatus in Fig. 166 is charged with pure 65% oleum, flask B with 100 g. of SCl₂ (see p. 370). Flask A is slowly heated in an H₂SO₄ bath, while B is cooled with an ice-water bath. The stoichiometric quantity of SO₃ is thus gradually distilled onto the SCl₂. The reaction proceeds with SO₂ evolution (use a hood!). Partial solidification of the flask contents frequently occurs at the beginning. However, the contents should again be completely liquid when the addition is completed. If necessary, the flask is heated at the end for a short time on a water bath. Flask A is then disconnected, the ground joint at C is stoppered, and the mixture is slowly distilled through a column (use a hood!). The mixture must be protected from contact with atmospheric moisture. The middle fraction is further purified by repeated careful fractionation, with S added to the distillation charge in order to convert all sulfur chlorides present to S₉Cl₂. The contents are distilled through an efficient column until a completely colorless product, coming over at 76-77°C, is obtained. The yield is about 80% of theoretical.

II. \[\text{PCl}_5 + \text{SO}_2 = \text{POCl}_3 + \text{SOCl}_2\]

<table>
<thead>
<tr>
<th></th>
<th>208.27</th>
<th>64.07</th>
<th>153.35</th>
<th>118.98</th>
</tr>
</thead>
</table>

A well-dried, 250-ml., two-neck, round-bottom flask, equipped with a reflux condenser connected to a CaCl₂ tube, is loaded with 100 g. of PCl₅. Sulfur dioxide is introduced through a gas inlet tube extending to the bottom of the flask. The SO₂ is carefully
Fig. 166. Preparation of thionyl chloride.

predried by allowing it to bubble through two wash bottles containing concentrated H₂SO₄. The reaction, which can be accelerated by shaking the flask, is complete after several hours, when all the PCl₅ dissolves.

The products are separated by repeated careful fractionation, using an efficient column. B.p. of SOCl₂, 77°C; of POCl₃, 108°C.

This preparation is generally not completely free of phosphorus compounds. The yield of SOCl₂ is 30 g. (50% of theoretical).

PROPERTIES:
Colorless, highly refractive liquid with an unpleasant, SO₂-like odor. M.p. —104.5°C, b.p. 77°C; d₃⁰ 1.64. Significant dissociation to S₂Cl₂, SO₂ and Cl₂ occurs just above the boiling point. Hydrolyzes in water to SO₂ and HCl; soluble in benzene and chloroform.

REFERENCES:

**Sulfuryl Chloride**

SO₂Cl₂

I. SO₂ + Cl₂ = SO₂Cl₂
64.07  70.91  134.98

a) The reaction proceeds very smoothly and almost quantitatively when activated charcoal is used as the catalyst.
The reactor is a bulb-type condenser with at least six bulbs. Each bulb is approximately half filled with loose glass wool, on top of which there is a layer of granular activated charcoal which occupies less than half of the remaining space. The condenser is clamped vertically; the lower end passes through a rubber stopper and into a suction flask (500-1000 ml.) with its side arm connected to a CaCl$_2$ tube in order to protect the contents against atmospheric moisture. Tank Cl$_2$ and SO$_2$ are used, if possible, since this is the simplest way to keep the flow rates constant over long periods. The gases are dried separately by passage through wash bottles filled with concentrated H$_2$SO$_4$. These bottles also serve as bubble counters. The gases are then mixed in a Y piece and fed into a flask in which the mixing is completed. When all the air is displaced, the outlet tube of this flask is tightly joined to the upper end of the reactor by means of a rubber stopper. The reactor is well cooled with externally flowing water. At flow rates of 3-4 bubbles/second in both wash bottles, the first SO$_2$Cl$_2$ drops begin to collect in the suction flask after 20-30 minutes. (The induction period can be shortened by moistening the uppermost sphere with a few milliliters of SO$_2$Cl$_2$.) From then on, about 150 g. of SO$_2$Cl$_2$ is formed per hour. This amount can be increased by increasing the flow rate. The product obtained is quite pure and needs to be fractionated only once at atmospheric pressure, which decreases the yield only slightly.

b) The reaction also proceeds smoothly when camphor is used as the catalyst.

A 500-ml., two-neck, ground-joint flask is provided with a CaCl$_2$ tube and a gas inlet tube reaching to the bottom. A tee connection allows simultaneous introduction of SO$_2$ and Cl$_2$.

Coarse camphor (10 g.) is placed in the flask, and well-dried SO$_2$ is passed through until the camphor is saturated and liquefies (1 part of camphor absorbs about 0.88 parts by weight of SO$_2$ at 725 mm.). Dried Cl$_2$ is then introduced; it is absorbed by the liquid, forming a colorless solution. After saturation, the SO$_2$ is reintroduced, followed by renewed passage of Cl$_2$. After the formation of approximately 30 g. of sulfuryl chloride, both gases may be introduced simultaneously.

When enough SO$_2$Cl$_2$ has been prepared, it is distilled on a water bath. The product obtained in the first distillation still contains camphor, which may be removed by careful fractionation.

II.

\[
2 \text{HSO}_2\text{Cl} = \text{SO}_2\text{Cl}_2 + \text{H}_2\text{SO}_4
\]

An ordinary combustion tube is half filled with pure chlorosulfonic acid (for preparation, see p. 385), is sealed off in the usual
way and is then heated in a paraffin or oil bath for 20 hours at 200-210°C. The initially water-clear liquid takes on a greenish color on cooling. The tube is opened with the usual precautions, the liquid is rapidly poured into a flask, and the fraction boiling below 110°C is distilled off. This fraction is redistilled on a water bath and the fraction boiling below 73°C is collected; it consists mainly of SO₂Cl₂. To remove HSO₃Cl and H₂SO₄, the product is poured into a separatory funnel filled with crushed ice and is briefly shaken; the lower, cloudy organic layer is removed. This layer is dried for some time in a desiccator over P₂O₅ and is finally re-distilled on a water bath at atmospheric pressure. The middle fraction, boiling between 69 and 70°C, is pure SO₂Cl₂. The yield is about 40%.

**PROPERTIES:**

Colorless, very mobile liquid; yellows slightly on prolonged standing because of partial dissociation; fumes somewhat in air; extremely pungent odor. M.p. -54.1°C, b.p. 69.2°C; d₄° 1.667. Decomposes gradually in water to form H₂SO₄ and HCl; under certain circumstances, decomposes explosively with alkalis. Soluble in benzene and toluene.

**REFERENCES:**

I. a) J. Meyer, Angew. Chem. 44, 41 (1931); see also H. Danneel, Angew. Chem. 39, 1553 (1926).

II. P. Behrend, J. prakt. Chem. 15, 23 (1877).

**Chlorosulfonic Acid**

\[ \text{HSO}_3\text{Cl} \]

\[
\begin{align*}
\text{SO}_3 & + \text{HCl} = \text{HSO}_3\text{Cl} \\
80.07 & \quad 36.47 \quad 116.54
\end{align*}
\]

A round-bottom flask, closed with a three-hole rubber stopper, is half filled with oleum of the highest SO₃ concentration possible. A gas inlet tube, reaching to the bottom of the flask, passes through one of the holes of the stopper, a thermometer through the second and a downward condenser ending in a CaCl₂ tube through the third. At the beginning of the run, the flask is inclined so that the condenser points upward. Thus, all products condensing during the reaction flow back into the flask. A slow, carefully dried HCl stream (see p. 280) is then passed through the oleum at room
temperature until no further absorption takes place. The condenser is then returned to its downward position and the flask contents are distilled in the HCl stream. The reaction must be protected against atmospheric moisture. The fraction coming over between 145 and 160°C is refractionated in the same manner in a clean apparatus with ground glass connections. A colorless distillate, stable for long periods of time, can be obtained only in the complete absence of organic substances (rubber, cork, dust, etc.). The boiling point of the pure middle fraction is 151-152°C. The yield is almost quantitative, based on the SO₃ content of the oleum.

Because of slight dissociation on heating, the product contains some dissolved HCl and SO₃, as well as traces of SO₂, Cl₂, SO₂Cl₂ and H₂SO₄ formed from the above. Completely pure HSO₃Cl is obtained by fractional crystallization in liquid nitrogen in complete absence of moisture. (For more details, see the original literature.)

PROPERTIES:

Colorless liquid, fuming strongly in moist air; pungent odor. M.p. -80°C, b.p. 152°C; d (20°C) 1.79.

Decomposes violently with water to form HCl and H₂SO₄.

REFERENCES:


Pyrosulfuryl Chloride

\[ \text{S}_2\text{O}_3\text{Cl}_2 \]

\[ 2 \text{SO}_3 + \text{CCl}_4 = \text{S}_2\text{O}_3\text{Cl}_2 + \text{COCl}_2 \]

The apparatus, consisting of a one-liter flask equipped with a long reflux condenser topped with a drying tube, is set up under an efficient hood because of the ensuing COCl₂ evolution. Commercial SO₃ (300 g.) is placed in the flask and CCl₄ (572 g.) is poured over it. The reaction rate is very low while the flask contents are cold. The flask is carefully heated on a sand bath until all the SO₃ dissolves and the brown liquid which forms no longer evolves any COCl₂. The reaction usually ends in two hours. The contents of the flask are then slowly distilled through a column protected from atmospheric moisture (use a hood!) and the fraction boiling between
135 and 160°C, consisting of crude $S_2O_5Cl_2$ contaminated with some $HSO_3Cl$, is collected separately. To purify the compound, small pieces of ice are added while the flask is rapidly rotated and efficiently cooled with an ice-salt bath; the ice vigorously hydrolyzes the $HSO_3Cl$, evolving $HCl$, while the $S_2O_5Cl_2$ is not attacked to any significant extent. As soon as the gas evolution subsides, the addition of ice is stopped, the flask is allowed to stand for several hours in the cooling bath, and the cold liquid, which by then has separated into two layers, is poured into a separatory funnel. Here the $S_2O_5Cl_2$ may become either the upper or the lower layer since the densities of the two phases are very similar. However, a separation with $S_2O_5Cl_2$ collecting in the bottom layer is easily attained by addition of some concentrated $H_2SO_4$ or cold water. The product is dried with $P_2O_5$ and distilled, while carefully protected from atmospheric moisture, at atmospheric pressure. The fraction distilling between 150 and 153°C is refractionated at reduced pressure. The yield is about 240 g. of pure $S_2O_5Cl_2$.

PROPERTIES:

Colorless, very mobile liquid; characteristic odor; fumes faintly in moist air and becomes cloudy because of the separation of sulfuric acid. M.p. $-37°C$, b.p. 152-153°C with slight decomposition; dissociates into $SO_3$, $SO_2$ and $Cl_2$ on prolonged refluxing or heating to 250°C; $d_5^0 1.84$; $d_2^0 1.87$.

Hydrolyzes in water, particularly when warm, to $H_2SO_4$ and $HCl$.

REFERENCES:


**Thionyl Bromide**

$SOCl_2$

$$SOCl_2 + 2HBr = SOBr_2 + 2HCl$$

Pure $SOCl_2$ (50 ml.) (see p. 382) is placed in a 150-ml. ground glass flask provided with a gas inlet tube reaching to the bottom and sealed in at the side. The flask is equipped with a reflux condenser closed off with a $CaCl_2$ drying tube. A moderately rapid stream of carefully dried $HBr$ is bubbled through for 12 hours while
the flask is cooled with ice. The contents gradually turn reddish. At the end of the reaction, the product mixture is distilled in ground glass apparatus at 62 mm.; about 50 ml. of orange-red crude SOBr₂ distills between 69 and 70°C. This crude is re-fractionated at 20 mm.; b.p. of the pure orange-yellow substance is 48°C. The yield is nearly quantitative.

Stored in sealed glass ampoules or in flasks with very tight ground glass stoppers.

Other preparative methods:

II. Reaction of SO₂ with Br₂ in the presence of PCl₃: 64 g. of SO₂ is added to a mixture of 138 g. of PCl₃ and 160 g. of Br₂, while the reactor is cooled. The yield, after fractional distillation, is 180 g. of SOBr₂.

III. When 1 mole of SOCl₂ is added dropwise to a solution of 2.1 moles of KBr in 150 ml. of liquid SO₂, SOBr₂ separates as a white precipitate. After evaporation of the SO₂, the product is distilled at 20°C and 0.1 mm. into a trap at −80°C. The yield is about 50%.

PROPERTIES:

Orange-yellow liquid. On prolonged standing, slowly decomposes into SO₂, Br₂ and S₂Br₂ and turns reddish; very sensitive to moisture. M.p. −49.5°C. Its thermal stability is poor and therefore SOBr₂ can be distilled only in vacuum. d. (20°C) 2.685.

Hydrolyzes in water to HBr and SO₂. Soluble in CS₂, C₆H₆, CHCl₃ and CCl₄.

REFERENCES:


II. German Pat. 665061 (1936) I. G. Farbenindustrie.


**Peroxymonosulfuric Acid**

\[
\text{H}_2\text{SO}_5
\]

\[
\text{HSO}_3\text{Cl} + \text{H}_2\text{O}_2 = \text{H}_2\text{SO}_5 + \text{HCl}
\]

116.34 34.02 114.08 36.47

A slight excess of 100% (or at least nearly anhydrous) H₂O₂ (see p. 140) is slowly added to pure, thoroughly cooled chloro-
sulfonic acid (see p. 385). Vigorous evolution of HCl occurs. When all the H₂O₂ has been added and the gas evolution has subsided, the reaction mixture is gradually warmed and the dissolved or still evolving HCl is removed in aspirator vacuum. The mixture cannot be allowed to stand too long prior to HCl removal because the H₂SO₅ tends to oxidize the HCl to Cl₂ and to oxides of chlorine. The HCl-free liquid can then be crystallized in a well-sealed flask. If, after standing for some time at room temperature, it is still not solid, the flask is placed in a cooling bath. After 12 hours the crystals are separated from the mother liquor either by rapid suction filtration on a glass frit or by centrifuging in the apparatus shown in Fig. 103 (p. 141). The effectiveness of this separation determines the purity of the product, which is normally 94-97%. The impurities present are H₂S₂O₅ and traces of Cl. The substance can be further purified by partial remelting. The yield is 50-70%. A small additional purified fraction can be obtained from the mother liquor. The handling of large quantities of H₂SO₅ is somewhat dangerous. Local overheating, caused, for example, by addition of H₂O, can cause explosive decomposition. Safety glasses should always be worn.

SYNONYMS:

Hypersulfuric acid, Caro's acid.

PROPERTIES:

Colorless, beautiful crystals; hygroscopic; pure material stable for a few days, although with slight loss of active oxygen, the rate of decomposition is catalysed by the impurities formed; vigorous oxidizing agent. M.p. +45°C with slight decomposition.

Small amounts of H₂SO₅ dissolve in ice water without evolving oxygen or hydrolyzing. When larger amounts are used and the water is at room temperature, H₂O₂ and H₂SO₄ are formed. Readily soluble in alcohol and ether.

REFERENCES:

J. D'Ans and W. Friederich, Ber. dtsch. chem. Ges. 43, 1880 (1910); Z. anorg. allg. Chem. 73, 325 (1912).

**Peroxydisulfuric Acid**

\[ H₂S₂O₈ \]

1. \[ 2 \text{HSO}_3\text{Cl} + \text{H}_2\text{O}_2 = \text{H}_2\text{S}_2\text{O}_8 + 2 \text{HCl} \]

Pure chlorosulfonic acid (see p. 385) is mixed slowly and with efficient cooling with the stoichiometric quantity of 100% H₂O₂.
(see p. 140 for preparation). The reaction proceeds with HCl evolution, which continues for some time after the end of the addition. When the gas evolution subsides, the solution is gradually heated, and both the dissolved and evolving HCl are removed with an aspirator. The liquid is allowed to stand in a closed flask; it usually solidifies slowly after some time at room temperature. The crystallization can be accelerated by cooling or seeding. The HCl evolution resumes during crystallization because the mother liquor becomes enriched with HSO₃Cl and H₂SO₅. After 12 hours, the solid acid is quickly suction-filtered through a glass frit or is isolated by centrifuging in the apparatus shown in Fig. 103 (p. 141). The purity is 92-98%; the yield is 60% of theoretical. A fair amount of a somewhat less pure fraction may still be obtained from the mother liquor by lower cooling.

II. Aqueous solutions of H₂S₂O₅ are obtained by electrolysis of concentrated H₂SO₄ solutions at a high current density and low temperature. For details, see the original literature.

SYNONYMS:
Hypersulfuric acid, persulfuric acid.

PROPERTIES:
Colorless, finely crystalline substance; ozone odor; extremely hygroscopic; pure H₂S₂O₅ is stable for several weeks with only a slight loss of active oxygen, while the impure acid is considerably less stable; strong oxidizing agent. M.p. 65°C (dec.).

Dissolves in water, with fizzing and considerable decomposition, to yield H₂SO₅ and H₂O₂; soluble without decomposition in alcohol; less soluble in ether.

REFERENCES:
I. J. D'Ans and W. Friederich, Ber. dtsh. chem. Ges. 43, 1880 (1910); Z. anorg. allg. Chem. 73, 325 (1912).

Ammonium Peroxydisulfate
(NH₄)₂S₆O₈

Prepared by anodic oxidation of a saturated (NH₄)₂SO₄ solution:

\[ 2(NH₄)₂SO₄ - 2 \epsilon = (NH₄)₂S₆O₈ + 2NH₄^+ \]

A clay cup with a capacity of 130 to 150 ml. is placed in a 500-ml. beaker of equal height. The cup is surrounded with a coil of
lead tubing which serves both as a cathode and a cooling coil. The current lead is a copper wire soldered to the coil. A 0.05-cm.-thick Pt wire spiral anode, ignited prior to the run, is suspended in the middle of the cup. A mixture of equal weights of concentrated \( \text{H}_2\text{SO}_4 \) and \( \text{H}_2\text{O} \) is used as the cathode liquid; the anode space is filled with an iron-free \( (\text{NH}_4)_2\text{SO}_4 \) solution, saturated at 10\(^\circ\)C [76.3 g. of \( (\text{NH}_4)_2\text{SO}_4 \) in 100 g. of \( \text{H}_2\text{O} \)].

The cooling water flow is turned on, and the electrodes are connected through a rheostat and an ammeter to the 12-14 v. power supply. The current should be 2.5 amp, and the electrolyte temperature as low as possible. Slight evolution of \( \text{O}_2 \) can be observed at the anode; simultaneously, an ozone odor is apparent. After 4-6 hours, white crystalline \( (\text{NH}_4)_2\text{S}_2\text{O}_8 \) separates in the clay cup. The electrolysis is continued for some time and then the salt is suction-filtered on fritted glass. The remaining mother liquor is largely removed by pressing on clay. The product still contains a few percent of sulfate. To purify the compound, it is recrystallized (from as small an amount of water as possible) by dissolving at 40\(^\circ\)C and then cooling an ice bath. The pure substance (negative test with \( \text{BaCl}_2 \)) is dried on clay and in the desiccator. After 10 hours of electrolysis the yield is 33 g.

The anolyte liquid, saturated with \( (\text{NH}_4)_2\text{S}_2\text{O}_8 \), can be remixed with fresh \( (\text{NH}_4)_2\text{SO}_4 \) and reelectrolyzed. The catholyte is gradually neutralized by \( \text{NH}_4^+ \) and therefore must be tested with pH paper and replaced with fresh acid when necessary. After 3-4 hours, another 20-40 g. of \( (\text{NH}_4)_2\text{S}_2\text{O}_8 \) is obtained.

**SYNONYM:**
The older name is ammonium persulfate.

**PROPERTIES:**
Colorless, platelike or prismatic crystals; stable for months when pure and dry; decomposes in the presence of moisture, gradually evolving ozone-containing oxygen; strong oxidizing agent. Decomposes on heating, evolving \( \text{O}_2 \) and forming \( (\text{NH}_4)_2\text{S}_2\text{O}_7 \). d 1.98.

Solubility (0\(^\circ\)C): 58.2 g.; (15.5\(^\circ\)C) 74.8 g./100 g. \( \text{H}_2\text{O} \). The solution decomposes slowly at room temperatures and rapidly at higher temperatures, evolving \( \text{O}_2 \) and forming \( \text{NH}_4\text{HSO}_4 \). Monoclinic crystals, space group \( \text{C}_{2h}^1 \).

**REFERENCES:**
Potassium Peroxydisulfate

K\(_2\)S\(_2\)O\(_8\)

Prepared by electrolytic oxidation of saturated KHSO\(_4\) solution:

\[
2 \text{KHSO}_4 - 2 e^- = \text{K}_2\text{S}_2\text{O}_8 + 2 \text{H}^+
\]

A 500-ml. battery jar, placed in a larger container which has an inlet and an outlet for cooling water, is used as the electrolysis vessel. The 1.4 × 4 cm. anode, a shiny Pt sheet, is suspended in the middle. Two Pt wire-gauze cathodes having over-all surface areas of 15 cm\(^2\) each are attached parallel to the anode, one on either side. The cathode-anode distance is 1.5 cm.

Before the run, the anode is ignited and the jar filled with dilute H\(_2\)SO\(_4\) saturated with KHSO\(_4\). The electrodes are then connected through a rheostat and an ammeter with an 8-12 v. power supply. The anode current is adjusted to a density of 0.48 amp./cm\(^2\) (5.3 amp. for the given anode surface) and the electrolysis is carried out for a few hours with intensive external cooling. The temperature of the electrolyte should not exceed +7°. The liquid turns cloudy after 10-15 minutes, due to separation of K\(_2\)S\(_2\)O\(_8\). The salt gradually collects at the bottom of the vessel as a white, loose, very fine crystalline precipitate. It is suction-filtered (good vacuum) on fritted glass and washed with some water. Small amounts of occluded sulfuric acid are removed by repeated recrystallization from water at 30°C. The pure substance (negative test with BaCl\(_2\)) is dried by pressing on clay and in a desiccator over concentrated H\(_2\)SO\(_4\) or CaCl\(_2\). After three hours of electrolysis, the yield is 27 g., corresponding to an electrolytic yield of 34%.

SYNONYM:

The older name is potassium persulfate.

PROPERTIES:

Colorless prisms or platelike crystals; only the completely dry material is stable for long periods; decomposes in moist air, forming KHSO\(_4\); strong oxidizing agent. Evolves oxygen on heating. d 2.477.

Solubility in water (0°C): 1.62 g.; (10°C) 2.60 g.; (20°C) 4.49 g.; (30°C) 7.19 g. of K\(_2\)S\(_2\)O\(_8\)/100 g. of H\(_2\)O. The solution decomposes on prolonged standing, evolving O\(_2\) and forming KHSO\(_4\).

Triclinic crystals, space group C\(_1\).
A solution of 10 g. of Co(CH$_3$COO)$_2$·4H$_2$O in 60 ml. of water is mixed with 10.2 g. of solid Na$_3$S$_2$O$_4$ (Co : Na$_3$S$_2$O$_4$ = 1 : 1.5) while a fast stream of oxygen-free N$_2$ is passed through. A solution of 3.5 g. of NaHCO$_3$ in 50 ml. of H$_2$O (Co : NaHCO$_3$ = 1 : 1.1) is then gradually added in small portions. The cobalt salt solution turns red-brown, and a brown, finely powdered precipitate of CoSO$_2$·3H$_2$O separates, while CO$_2$ is evolved. The precipitate is rapidly suction-filtered in a nitrogen atmosphere, washed with water, alcohol and ether, and dried on clay in an evacuated desiccator previously flushed with N$_2$.

**Properties:**

Brown powder. Decomposed by atmospheric oxygen or heat, forming cobalt sulfide. Soluble in NH$_3$, pyridine and ethylenediamine, forming deep dark-red solutions.

**Reference:**


**Sodium Dithionite**

Na$_2$S$_2$O$_4$·2H$_2$O

Sodium dithionite dihydrate is prepared by salting out an aqueous solution of commercial Na$_2$S$_2$O$_4$.

*This refers to 100% Na$_2$S$_2$O$_4$; commercial products are usually less pure.*
A 20-25% solution of the purest obtainable Na$_2$S$_2$O$_4$ in air-free distilled H$_2$O is prepared in an inert gas atmosphere. The solution is filtered in the absence of air. Then 30 g. of finely powdered NaCl per 100 ml. of H$_2$O is quickly added and immediately vigorously shaken. After about half a minute, the dihydrate precipitates as a thick, white crystalline slurry. It is suction-filtered (again in the absence of air) and washed with saturated NaCl solution, then with aqueous and finally with anhydrous acetone. The crystals are dried on clay in an evacuated desiccator prefilled with nitrogen. Other salting-out agents include NaHSO$_3$, NaOH, NaNO$_2$, CH$_3$COONa, MgCl$_2$, CaCl$_2$ and ZnCl$_2$.

Because of its instability, the dihydrate has no practical uses; anhydrous Na$_2$S$_2$O$_4$ is used on a large scale as a reducing agent in the dye industry, for preparing rongalite (CH$_2$O·Na·HSO$_2$·H$_2$O) and as an O$_2$ absorbent.

SYNONYM:

The older designation is "sodium hyposulfite," while in industry it is called (incorrectly) "sodium hydrosulfite."

PROPERTIES:

Formula weight 192.13. Colorless, needle-shaped crystals; very air sensitive; decomposes particularly easily when moist, forming Na$_2$S$_2$O$_5$ and Na$_2$S$_2$O$_3$; strong reducing agent. Decomposes thermally to Na$_2$S$_2$O$_3$, Na$_2$SO$_3$ and SO$_3$.

Readily soluble in water (2.18 g. of Na$_2$S$_2$O$_4$·2H$_2$O/100 g. of H$_2$O at 20°C); insoluble in ethanol.

REFERENCE:

K. Jellinek, Z. anorg. allg. Chem. 70, 93 (1911).

**Zinc Dithionite**

$$\text{ZnS}_2\text{O}_4$$

$$\text{Zn} + 2\text{SO}_2 = \text{ZnS}_2\text{O}_4$$

65.38 128.13 193.51

A two-liter round-bottom flask with a side arm reaching to the bottom and serving as gas inlet tube is used as the reactor. The flask carries an Anschütz attachment with a mercury-seal stirrer in one opening, while the other is closed with a one-hole rubber stopper with a cotton plug in the hole. In this manner a steady, positive SO$_2$ pressure is maintained in the flask.
The flask is charged with 750 ml. of ethanol, 250 ml. of H₂O and 270 g. of finely powdered, high-grade Zn dust. With vigorous stirring, 470 g. of pure SO₂ is introduced at 60°C. The reaction is exothermic. After a short time, a paste of coarsely crystalline ZnS₂O₄ begins to separate. When the reaction is complete, the mixture is allowed to cool and is then rapidly suction-filtered in a fast H₂ stream. The crystals are washed with absolute ethanol and dried in vacuum at 60-70°C. Acetone may be used for the washing. The yield is nearly quantitative but depends essentially on the composition of the zinc dust. The latter may be activated, if desired, by pretreatment with very dilute AgNO₃ solution.

SYNONYM:

The older designation is “zinc hyposulfite,” while in industry it is frequently called “zinc hydrosulfite.”

PROPERTIES:

White, crystalline powder; SO₂ odor, due to decomposition on standing in air (SO₂ evolution); strong reducing agent. Readily soluble in water (the ratio is about 1 : 7) with a strong tendency to form supersaturated solutions.

REFERENCES:

German patent 218192 (1907) Badische Anilin- und Soda Fabrik; Chemiker-Ztg. Rep. 31, 324 (1907).

**Sodium Dithionate**

\[ \text{Na}_2\text{S}_2\text{O}_4 \cdot 2\text{H}_2\text{O} \]

I. \[ \text{MnO}_2 + 2\text{SO}_2 = \text{MnS}_2\text{O}_4 \]

<table>
<thead>
<tr>
<th></th>
<th>(86.93)</th>
<th>(128.13)</th>
</tr>
</thead>
</table>

\[ \text{MnS}_2\text{O}_4 + \text{Na}_2\text{CO}_3 = \text{Na}_2\text{S}_2\text{O}_4 + \text{MnCO}_3 \]

<table>
<thead>
<tr>
<th></th>
<th>(106.00)</th>
<th>(242.16)</th>
<th>(114.94)</th>
</tr>
</thead>
</table>

A one-liter round-bottom flask equipped with a stirrer, a thermometer and a gas inlet tube reaching to the bottom is used as the reactor. The flask is cooled in an ice bath and 500 ml. of H₂O is saturated with very pure SO₂. While the contents are vigorously stirred and the addition of SO₂ is continued, 80 g. of finely powdered, very pure MnO₂ is added in portions of 1-2 g. over a period
of 2.5-3 hours; the temperature of the mixture should not exceed 10°C. The stirring is continued for some time after the addition until there is no further color change. Excess SO₃ is removed in vacuum, while the flask is gently heated to 40°C. The gelatinous residue is filtered and washed with warm water.

The filtrate is combined with the wash water and stirred at 35-40°C with solid BaCO₃ until there is no further evolution of CO₂. The stirring is continued for another 10 minutes. The mixture is then neutralized to litmus with solid Ba(OH)₂. To test for completeness of removal of sulfate and sulfite, a filtered sample of the liquid is mixed with dilute HCl and BaCl₂ solution. If a precipitate is still formed, more hot saturated Ba(OH)₂ solution is added and the test is repeated. When the result is negative, the solution is suction-filtered and the precipitate washed with 50 ml. of water.

Approximately 65 g. of Na₂CO₃ is slowly added, in portions of 1-2 g., to the filtrate at 35°C. The mixture is vigorously stirred and the temperature increased to 45°C. As soon as a continuous test with litmus paper indicates a lasting, definitely alkaline reaction, addition of the Na₂CO₃ is interrupted and the mixture is suction-filtered and washed with 150 ml. of 50°C water containing some Na₂CO₃. The filtrate is retested with litmus paper and, if necessary, mixed with further Na₂CO₃ and filtered. The solution is concentrated on the water bath to a much smaller volume (discarding any precipitate which might separate at the beginning) and is then allowed to stand for some time at 10°C. The separated Na₂S₂O₆·2H₂O is suction-filtered (good suction, no washing) and dried by pressing on clay. Concentrating the solution too much causes contamination with Na₂CO₃. The yield is 88%, based on MnO₂ used.

\[
\begin{align*}
\text{II.} & \quad \text{a) } \text{BaS}_2\text{O}_6 + \text{Na}_2\text{CO}_3 &= \text{Na}_2\text{S}_2\text{O}_6 + \text{BaCO}_3 \\
& \quad (2 \text{H}_2\text{O}) & \quad (2 \text{H}_2\text{O}) & \quad 333.52 & \quad 106.00 & \quad 242.16 & \quad 197.37 \\
& \quad \text{b) } \text{BaS}_2\text{O}_6 + \text{Na}_2\text{SO}_4 &= \text{Na}_2\text{S}_2\text{O}_6 + \text{BaSO}_4 \\
& \quad (2 \text{H}_2\text{O}) & \quad (2 \text{H}_2\text{O}) & \quad 333.52 & \quad 142.05 & \quad 242.16 & \quad 233.42 \\
\end{align*}
\]

A hot solution of BaS₂O₆·2H₂O is mixed with the stoichiometric quantity of Na₂CO₃ or Na₂SO₄, also dissolved in hot water. After boiling for several hours, the precipitate is filtered off and the solution concentrated. Isolation and drying of the crystals is the same as in method I.

PROPERTIES:

Colorless, water-clear crystals; very stable in air. On heating, the water of crystallization is given off between 60 and 100°C;
above 200°C quantitative decomposition into Na₂SO₄ and SO₂.

Readily soluble in water (at 0°C, 6.05; at 20°C, 13.39; at 30°C, 17.32 wt. % of salt is dissolved); insoluble in alcohol.

REFERENCES:

**Barium Dithionate**

BaS₂O₆·2H₂O

\[
\begin{align*}
\text{MnO}_2 + 2 \text{SO}_2 &= \text{MnS}_2\text{O}_8 \\
86.93 & \quad 128.13 \\
\text{MnS}_2\text{O}_8 + \text{Ba(OH)}_2 &= \text{BaS}_2\text{O}_8 + \text{Mn(OH)}_2 \\
(8\text{H}_2\text{O}) & \quad (2\text{H}_2\text{O}) \\
315.51 & \quad 333.52 \\
& \quad 88.95
\end{align*}
\]

A solution of MnS₂O₈ is prepared from sulfurous acid and MnO₂ in the manner described for Na₂S₂O₅·2H₂O (see above). The filtered clear solution is heated to 25-40°C and stirred with 160 g. of Ba(OH)₂·8H₂O over a period of 30 minutes. Stirring is continued for 30 minutes after completion of the reaction. The solution is then heated to 65-75°C and enough base is added to make the mixture strongly alkaline. Very vigorous agitation is necessary during the addition of the base. The heating and agitation are continued for another 30 minutes. The separated hydrated oxide is filtered hot and washed with 300 ml. of Ba(OH)₂ solution held at 65°C. The wash water is combined with the filtrate and retested for alkalinity. If the alkaline reaction is weak, more Ba(OH)₂·8H₂O is added and the solution is refiltered. The excess base is then precipitated with CO₂ and filtered off. The solution is concentrated on a steam bath to about 50 ml. and cooled to crystallize. The BaS₂O₆·2H₂O precipitate is suction-filtered (the best vacuum possible—no washing!) and freed of traces of mother liquor by pressing on clay. Additional salt may be precipitated from the mother liquor by the addition of 75 ml. of ethanol. The yield is 73%, based on MnO₂ used.

**PROPERTIES:**

Colorless, monoclinic, prismatic crystals; stable in air. On heating, the water of crystallization is given off at 120°C. Significant
decomposition starts at 140°C (SO₂ evolution and formation of BaSO₄).

Readily soluble in water (at 0°C, 7.86; at 20°C, 15.75; at 30°C, 19.86 wt. % of salt is dissolved); insoluble in alcohol.

REFERENCE:

Potassium Trithionate
K₂S₃O₆

I.

\[ 2 \text{KHSO}_3 + \text{SCl}_2 = \text{K}_2\text{S}_3\text{O}_6 + 2 \text{HCl} \]

\[ \begin{array}{ccc} 240.34 & 102.98 & 270.39 & 72.93 \end{array} \]

Sulfur dioxide is bubbled through 800 ml. of cooled 5M potassium hydroxide solution until the solution is converted to KHSO₃ (pH ~ 7). In the meantime, a solution of 100 g. of SCl₂ in 1.5 liters of pure petroleum ether is precooled to -20°C. The KHSO₃ solution is cooled to -5°C. It is then mixed in a 3- to 4-liter stoppered flask with 200-ml. portions of the SCl₂ solution. The liquid turns yellow in the process and must be decolorized before each new addition by thorough shaking. The temperature of the mixture should not rise above +10°C during the reaction. At the end of the addition the mixture is allowed to stand for some time at 0°C in order to complete the separation of the trithionate. The crystalline slurry is suction-filtered, washed with acetone, and dried on clay dishes at room temperature. The yield is 120 g. of approximately 86% K₂S₃O₆, but the product is still contaminated with KCl and sulfur. To recrystallize the salt, it is dissolved in about 350 ml. of H₂O at 35°C, and the solution is filtered through a heated funnel and rapidly cooled to 0°C (longer heating or higher temperature must be avoided because of the instability of K₂S₃O₆). Completely pure K₂S₃O₆ separates. By precipitating the mother liquor with an equal volume of acetone and renewed cooling to 0°C, an additional fraction of the same purity can be obtained. The crystals are filtered with strong suction, washed with acetone, and dried by pressing on clay at room temperature. The yield is 85 g.

II. REACTION OF SO₂ WITH AQUEOUS K₂S₂O₃ SOLUTION

Saturated sulfuric acid (20 ml.) is added to 200 ml. of saturated K₂S₂O₃ solution at 30°C. The flask must be thoroughly cooled with
running water. The initial yellow color of the solution disappears after some time. The addition is then repeated, using gaseous SO₂, until a strong yellow color is apparent. The solution is allowed to stand until the color disappears, and the process is repeated until the yellow color of the solution persists for a fairly long period. After standing for several hours at about 10°C, the precipitated pale yellow crude product is suction-filtered and thoroughly washed with alcohol. To purify the crude compound, it is dissolved in some water and filtered free of suspended S, and pure K₂S₃O₆ is precipitated as shiny needles by mixing the filtrates with an approximately equal quantity of alcohol. The salt is suction-filtered, washed with alcohol and dried on clay at room temperature.

**PROPERTIES:**

Colorless crystals with a salty, bitter taste; the pure, dry salt is stable for a fairly long time. Rapidly decomposes into SO₃, S and K₂SO₄ on heating to 30-40°C. d. 2.33.

Readily soluble in water; 100 g. of solution contains 8.14 g. of K₂S₃O₆ at 0°C, 18.43 g. at 20°C; the solution decomposes slowly into K₂S₃O₆ and SO₂. Insoluble in alcohol.

Crystallizes in K₅ structure type.

**REFERENCES:**


**Potassium Tetrathionate**

K₂S₃O₆

I. \[2 \text{H}_2\text{SO}_3 + \text{S}_2\text{Cl}_2 = \text{H}_2\text{S}_4\text{O}_6 + 2\text{HCl}\]  
164.16 135.04

\[\text{H}_2\text{S}_4\text{O}_6 + 2\text{KOH} = \text{K}_2\text{S}_3\text{O}_6 + 2\text{H}_2\text{O}\]  
112.21 302.46

A two- to three-liter stoppered glass flask is used to saturate 750 ml. of H₂O with SO₂ at 0°C. Disregarding the appearance of any crystalline SO₃·6H₂O, the solution is reacted at 0°C with 100-ml. portions of a solution of 75 g. of S₂Cl₂ in 500 ml. of
petroleum ether precooled to $-15^\circ\mathrm{C}$. The liquid turns yellow in the process; it must be decolorized before the addition of a new portion by vigorous shaking, following which it is cooled to $0^\circ\mathrm{C}$. At the end of the addition, the mixture should still have an odor of $\mathrm{SO}_2$. The petroleum ether is removed in a separatory funnel, and a fast air stream is passed through the aqueous layer for several hours until no further odor of $\mathrm{SO}_2$ can be detected. The solution is then cooled to $0^\circ\mathrm{C}$ and neutralized with an ice-cold solution of 150 g. of KOH in one liter of aqueous alcohol (final pH 6-7). The precipitated $\mathrm{K}_2\mathrm{S}_4\mathrm{O}_6$, which still contains about 10% KCl, is suction-filtered and dried on clay at room temperature. The yield is about 165 g. To purify the crude product, it is dissolved in 120 ml. of 70°C water, thoroughly stirred, and, if necessary, reheated rapidly to 60°C. It is then filtered rapidly through a heated funnel; long heating or temperatures above 60°C must be avoided because of the instability of $\mathrm{K}_3\mathrm{S}_2\mathrm{O}_3$. On cooling to $0^\circ\mathrm{C}$, the filtrate yields 120 g. of 100% $\mathrm{K}_2\mathrm{S}_4\mathrm{O}_6$. The crystals are filtered by suction, washed with 150 ml. of aqueous alcohol, and dried by pressing on clay at room temperature. By adding the wash alcohol to the mother liquor, a further 20 g. of 99% pure salt can be precipitated.

II. \[2\mathrm{K}_2\mathrm{S}_4\mathrm{O}_6 + \mathrm{I}_2 = \mathrm{K}_3\mathrm{S}_2\mathrm{O}_3 + 2\mathrm{KI}\]

\[(1^{1/3}\mathrm{H}_2\mathrm{O})\]

An aqueous, nearly saturated solution of 39.5 g. of $\mathrm{K}_2\mathrm{S}_4\mathrm{O}_6 \cdot 1-2/3 \mathrm{H}_2\mathrm{O}$ (sulfate-free) is added very slowly (drop-by-drop) to an ice-cooled solution of 26 g. of $\mathrm{I}_2$ in a mixture of ethanol and a few milliliters of $\mathrm{H}_2\mathrm{O}$. Very vigorous stirring is needed during the addition. The reaction is instantaneous; the tetrathionate, which is insoluble in ethanol, separates as small crystals. At the end of the addition, the solution is suction-filtered and washed with alcohol until the wash liquor is free of iodine and iodide. To purify the salt, it is redissolved at room temperature in as little water as possible and precipitated with alcohol. The precipitate (small, shiny crystals) is completely pure. It is dried by pressing between filter papers and then in a desiccator over concentrated $\mathrm{H}_2\mathrm{SO}_4$.

PROPERTIES:

Colorless, platelike or prismatic crystals; the pure dry material is stable for a very long time without change but decomposes if $\mathrm{K}_2\mathrm{S}_2\mathrm{O}_3$ or occluded mother liquor is present, assuming a characteristic odor. On ignition, $\mathrm{K}_2\mathrm{S}_4\mathrm{O}_6$ decomposes to $\mathrm{K}_2\mathrm{SO}_4$, $\mathrm{SO}_2$ and $\mathrm{S}$. $d$ 2.29.

Readily soluble in water: 100 g. of solution at $0^\circ\mathrm{C}$ contains 12.60 g., at $20^\circ\mathrm{C}$, 23.18 g. of $\mathrm{K}_2\mathrm{S}_4\mathrm{O}_6$; the solution decomposes slowly to $\mathrm{K}_3\mathrm{S}_3\mathrm{O}_8$ and $\mathrm{K}_2\mathrm{S}_5\mathrm{O}_8$. Insoluble in absolute alcohol.
Monoclinic crystals, space group C-Cc.

REFERENCES:


Potassium Pentathionate

\[ K_2S_5O_6 \cdot 1.5 H_2O \]

I. \[ SCl_2 + 2 Na_2S_2O_3 = Na_2S_2O_6 + 2 NaCl \]
(3 H_2O)
\[
\begin{array}{ccc}
102.98 & 406.41 & 116.91 \\
\end{array}
\]

\[ Na_2S_2O_6 + 2 KCH_3COO = K_2S_5O_6 + 2 NaCH_3COO \]
(1.5 H_2O)
\[
\begin{array}{ccc}
196.28 & 361.55 & \\
\end{array}
\]

A solution of 51 g. of SCl_2 in 200 ml. of CCl_4 is prepared in a two-liter, stoppered, wide-neck flask and is then cooled to \(-15^\circ C\). At the same time, a solution of 250 g. of Na_2SO_3 \cdot 5H_2O in 400 ml. of water is prepared and placed in an ice bath. In a third vessel, 200 ml. of 36% hydrochloric acid is mixed with 200 ml. of water and is also cooled to \(0^\circ C\). The Na_2S_2O_3 solution and the hydrochloric acid are then rapidly and simultaneously poured into the SCl_2 solution; the flask is closed and vigorously shaken. The reaction temperature should not exceed \(0^\circ C\). The mixture becomes colorless almost immediately, or should become so within 20 sec., while the aqueous layer should show only a very slight turbidity due to S. Without delay, 120 ml. of 0.3M FeCl_3 solution, precooled to \(0^\circ C\), is then added until the aqueous phase is colored pale yellow. The dark color of the intermediate iron (III) thiosulfate complex is briefly evident and then disappears. The aqueous solution is then separated in a funnel and immediately concentrated at 12 mm. and a bath temperature of 35-40°C to about 170 ml. The residual NaCl is filtered off and the ice-cold concentrate is reacted with ice-cold methanolic potassium hydroxide solution (approximately 20 g. of KOH to 100 ml. of methanol). The alkaline solution is added drop-by-drop and the mixture must be continuously and vigorously stirred. The temperature should never rise above \(+10^\circ C\). The brown hydrated iron oxide formed on contact of the two solutions is immediately redissolved by the acid. When the greenish-black hydroxide intermediate begins to separate (pH \(\sim 3\)), the addition of
potassium hydroxide is interrupted and the solution is again cooled
to 0°C. The separated crystalline slurry is suction-filtered and
washed with acetone until the yellowish color disappears. The
product is dried on clay at room temperature. The yield is 102 g.
of 85% K₂S₅O₆·1.5H₂O, contaminated with KCl. To recrystallize it,
50 g. of the crude product is added to 100 ml. of 0.5N HCl at 60°C,
while the solution (which cools in the process) is rapidly reheated
to 50°C and filtered through a heated funnel. The clear solution is
placed in a dish set on ice. Star-shaped crystals of 100% pure
K₂S₅O₆·1.5H₂O separate; they are filtered by suction and, after
washing with alcohol, are dried on clay. The yield from the entire
batch is 46 g. On addition of methanol to the mother liquor, another
13 g. of 80% pure salt is obtained.

II. REACTION OF THIOSULFATE WITH HYDROCHLORIC ACID
IN THE PRESENCE OF ARSENIOUS ACID

A solution of 8-10 g. of As₂O₃ in 50% sodium hydroxide is pre-
pared and added to a solution of 500 g. of C.P. Na₂S₂O₃·5H₂O in 600
ml. of water. The reaction vessel is a five-liter flask; the mixture
is well stirred and cooled to —10°C (incipient crystallization). Then
800 ml. of concentrated hydrochloric acid (precooled to —15°C) is
poured in at once. After thorough mixing, the NaCl precipitate is
filtered off on a fritted glass suction filter. The clear filtrate is
allowed to stand in a loosely stoppered flask for 3-4 days at 25°C.
Considerable precipitation of S and As₂S₃ occurs. The solution is
passed through a finely porous filter and is immediately con-
centrated in vacuum to 200 ml. in a glass rotary evaporator at
38-40°C and 21 mm. (If no evaporator is available, the concentra-
tion can also be carried out with a small oil pump at 2-5 mm.; the
H₂O is condensed with an ice-salt or Dry Ice bath; the pump is
protected from acid vapors by a CaO drying tower.) The freshly
precipitated NaCl is filtered off; the concentrate (d. 1.6) is mixed
with 100 ml. of glacial acetic acid and cooled in a tall beaker to
—10°C. A thick slurry of fine KC₂H₃O₂ crystals is now added in
portions while the temperature is kept below —2°C and the mixture
is vigorously stirred. (The slurry is prepared by dissolving 80 g.
of pure, fused KC₂H₃O₂ in 250 ml. of boiling absolute ethanol,
cooling with agitation to room temperature and adding — also with
vigorous shaking — 50 ml. of glacial acetic acid.) The KC₂H₃O₂
dissolves because of its fine particle size, and spontaneous sepa-
ration of K₂S₅O₆·1.5H₂O occurs after 30-60 seconds. The crys-
tals are immediately suction-filtered (otherwise partial conversion
to K₂S₅O₆ occurs) and washed with a few milliliters of a mixture
of two parts of glacial acetic acid and one part of water, then
with aqueous alcohol, and finally with absolute ethanol. They are
dried by pressing on clay at room temperature. The yield is 80-100 g. of very pure K$_2$S$_5$O$_6$·1.5H$_2$O. Addition of a large amount of ethanol to the mother liquor yields another (95% pure) fraction.

**PROPERTIES:**

Colorless, prismatic or platelike crystals; the pure, dry material is stable for a long time; very unstable on contact with alkali. On heating, the water of crystallization is given off with simultaneous decomposition to K$_2$SO$_4$, SO$_2$ and S. d. 2.11.

Readily soluble in water; 100 g. of solution at 0°C contains 15.50 g. and at 20°C, 24.78 g. of K$_2$S$_5$O$_6$·1.5H$_2$O; the solution decomposes into K$_2$S$_4$O$_6$ and S. Insoluble in absolute alcohol.

**REFERENCES:**


**Potassium Hexathionate**

K$_2$S$_5$O$_6$

I. **REACTION OF THIOSULFATE WITH NITRITE IN ACID SOLUTION**

An aqueous solution of thiosulfate and nitrite is added in one portion and with strong agitation to a mixture of 200 ml. of concentrated hydrochloric acid and 100 ml. of water, precooled to −30 to −40°C, in a three-liter, round-bottom, wide-neck flask. The thiosulfate-nitrate solution is prepared by dissolving 12 g. of C.P. KNO$_3$ in a filtered solution of 90 g. of technical grade K$_2$S$_2$O$_3$ in 90 ml. of water. The mixture first turns dark brown; after a few seconds it becomes dark green and evolves NO vigorously; after 30 seconds the solution turns light green and then, over a period of 2-3 minutes, first yellow and finally a pure white. Until this happens, vigorous agitation is required since otherwise the polythionate solution decomposes with precipitation of sulfur. The nitrogen oxides still present are driven off with a fast N$_2$ stream and the solution is suction-filtered through glass frit to remove precipitated KCl.

The clear filtrate from two such batches is concentrated at 25-30°C and 15-18 mm. to a moderately thick slurry. The crystals
are filtered by suction on fritted glass, washed with aqueous and then absolute alcohol, and dried on clay at room temperature. The yield is 60-70 g. of approximately 60% $K_2S_6O_6$ contaminated primarily with $KCl$. To purify it, 50 g. of the crude product is heated in 75 ml. of 2N HCl to about 80°C, while the flask contents are vigorously swirled around. The clear, slightly yellow solution which forms is immediately cooled with shaking. The salt precipitate is suction-filtered, washed thoroughly with alcohol, and dried by pressing on clay. The yield from the two batches is 40-44 g. of pale yellow 97.5% $K_2S_6O_6$.

\[
S_2Cl_2 + 2Na_2S_2O_3 \xrightarrow{(HCl)} (5 H_2O) Na_2S_6O_6 + 2NaCl
\]

\[
\begin{align*}
\text{Na}_2\text{S}_6\text{O}_6 + 2\text{KCH}_3\text{COO} &= \text{K}_2\text{S}_6\text{O}_6 + 2\text{NaCH}_3\text{COO} \\
196.28 &+ 366.59 = 135.04 &+ 496.41
\end{align*}
\]

The reaction is completely analogous to that for the preparation of $K_2S_5O_4\cdot 1.5H_2O$ from $SCl_2$ and thiosulfate (see above). The details of that procedure can therefore be applied unless noted to the contrary. The two cold solutions (one of 100 g. of $Na_2S_2O_3 \cdot 5 H_2O$ in 150 ml. of water and the other of 80 ml. of 36% hydrochloric acid in 80 ml. of water) are added simultaneously to a solution of 27 g. of $S_2Cl_2$ in 100 ml. of $CCl_4$, precooled to $-15°C$ in a one-liter wide-neck flask. The mixture is shaken, whereupon the solution becomes colorless. Then about 15 ml. of 0.6M $FeCl_3$ solution is added until the aqueous layer turns slightly yellow. It is separated in a funnel, and the aqueous $Na_2S_6O_6$ solution is immediately concentrated at 35°C and 12 mm. to about 50 ml. The $NaCl$ precipitate is filtered off and the concentrate cooled to 0°C. Cold methanolic $KOH$ solution is added in drops and with stirring until a pH of 1-2 (use indicator paper) is attained. The crystalline slurry is suction-filtered, washed twice with 40-ml. portions of acetone, and dried on a clay dish. The yield is 42 g. of 81% $K_2S_6O_6$.

To purify, 20 g. of the crude product is dissolved in 30 ml. of 2N HCl; the clear solution is rapidly heated to 60°C and immediately cooled again in ice water, while occasionally swirled around. Filtering by suction, washing, and drying of the crystals are as in method I. The yield from a batch is about 22 g. of 96% $K_2S_6O_6$.

**PROPERTIES:**

Colorless to faintly yellow, copious microcrystalline powder which becomes electrostatically charged with slight friction; stable for a long time in dry air; readily decomposed by alkali.
Readily soluble in water (although often slowly); however, the initially clear solution soon decomposes to $K_2S_5O_6$ and S.

REFERENCES:

**Wackenroder Liquid**

This is a liquid prepared by passing $H_2S$ through an aqueous $SO_2$ solution. In addition to finely divided S and small amounts of $H_2SO_4$, it contains mostly higher polythioacids, particularly $H_2S_5O_6$. The component distribution varies greatly with the preparative conditions (rate of the $H_2S$ stream, reaction time, temperature of the solution, etc.).

In the Debus method, a slow stream of pure $H_2S$ gas is passed for 2-3 hours through 480 ml. of nearly saturated aqueous $SO_2$ solution held just above 0°C. After the reaction the liquid, which still retains a strong odor of $SO_2$, is allowed to stand in the dark for 1-2 days in a closed flask. The $H_2S$ treatment is then repeated in the same manner. This intermittent $H_2S$ treatment is continued for about 10-14 days until all of the $SO_2$ — including that formed during the reaction — is used up; this occurs when the mixture no longer gives off the odor of $SO_2$ after standing for 10-12 hours at room temperature. The liquid thus obtained is an emulsion. Its thick layers are opaque; thin ones are translucent and red. It can be concentrated on a water bath to $d$ 1.3, in vacuum to $d$ 1.46. No decomposition of the polythioacids occurs in either case, but S precipitates out. The concentrate may be stored in the dark for a long time.

REFERENCES:

**Polythionic Acids**

$H_5S_4O_9, H_6S_5O_4$

See the original literature for the preparation of these compounds.
REFERENCES:

Nitrosyl Hydrogen Sulfate

(NO)HSO₄

SO₂ + HNO₃ = (NO)HSO₄

64.07  63.02  127.09

Carefully dried SO₂ is introduced into a wash bottle cooled with an ice-salt bath and containing pure, fuming HNO₃ (d 1.60). The reaction is exothermic but the temperature should not rise above +5°C. The SO₂ flow is continued until a thick slurry of (NO)HSO₄ is separated, but some unreacted liquid nitric acid is still present. The crystals are rapidly filtered by suction through a fritted glass filter, washed with glacial acetic acid and CC1₄, and dried on clay in a desiccator over P₂O₅.

SYNONYM:
Nitrosyl sulfuric acid; in industry it is also called lead chamber crystals because of its occurrence as an impurity in the chamber process for manufacture of H₂SO₄.

PROPERTIES:
White, featherlike to flaky crystals; stable in dry air; sensitive to moisture. M.p. 73.5°C (dec.).
Decomposed by water into sulfuric and nitric acids; soluble without decomposition in concentrated H₂SO₄.

REFERENCES:

Tetrasulfur Tetranitride

S₄N₄

4 S + 6 Cl₂ + 16 NH₃ = S₄N₄ + 12 NH₄Cl

128.26  425.48  272.51  184.30  641.96

The strongly exothermic process is carried out in an inert organic solvent by reacting NH₃ with a solution (of known concentration) of Cl₂ in S₂Cl₂.
The reaction is carried out in a six-liter round-bottom flask with a three-hole cork stopper. The stopper holds a large-diameter inlet tube reaching as far down into the flask as possible; the tube has a T connection at the top through which a wire can be pushed to remove any plugs that may form. The inlet tube is connected with an NH$_3$ cylinder via a flow meter, a pressure release valve, and a long KOH drying tube. The reaction flask is also provided with a power-driven stirrer and a reflux condenser topped with a KOH drying tube.

Four liters of CCl$_4$ (dried over P$_2$O$_5$) and 250 ml. of S$_2$Cl$_2$ are placed in the flask. This solution is first saturated with Cl$_2$ at room temperature; then a fast stream of NH$_3$ (about 50 liters/hour) is passed through with vigorous stirring. The reaction temperature may not exceed 30-50°C; if necessary, the flask should be cooled with ice water.

A thick reddish-brown slurry quickly forms during the reaction. It gradually becomes grayish-green; after 3-4 hours the color becomes lighter. The slurry turns salmon-red after about six hours. At this point, the introduction of NH$_3$ should be stopped. The precipitate is suction-filtered on a large filter, shaken for 15 minutes with three liters of water, again collected on a frit, and dried on a clay plate. It is then again shaken for one hour with 750 ml. of ether in a one-liter powder bottle to dissolve the by-product S$_7$NH. After filtration and washing with ether, the residue is placed in an extraction tube and treated with dry dioxane at room temperature until the extract has only a slight yellow-orange color. The dioxane solution is carefully concentrated in vacuum. The brownish-red residue is taken up in hot benzene; on cooling, S$_4$N$_4$ crystallizes out in orange-red needles. For further purification, the substance can be sublimed in high vacuum at a bath temperature of about 100°C.

The yield varies; generally, it is about 100 g.

It must be kept in mind during the entire procedure that S$_4$N$_4$ is susceptible to explosive decomposition induced by shock or temperatures above 100°C.

PROPERTIES:

Light yellow-orange solid at ordinary temperature; becomes light yellow at $-30^\circ$C; on heating to 100°C, orange-red. M.p. 178°C, b.p. about 185°C; decomposes explosively on further heating; d 2.22.

Insoluble in water; readily soluble in many organic solvents such as benzene, CS$_2$ and dioxane; only moderately soluble in alcohol and ether.

Monoclinic crystals, type C$_{2h}$; space group P2$_1$/n.
The reaction vessel is a 500- to 750-ml. stirred autoclave which can be heated to 110°C. A mixture of 24 g. of \( \text{S}_4\text{N}_2 \) and 50 g. of S is dissolved or suspended in 380 ml. of pure \( \text{CS}_2 \) and heated in the autoclave for two hours at 110°C. The mixture is then cooled as rapidly as possible. If a great deal of thiocyanogen polymer forms during the reaction, it is filtered off. The residue is thoroughly washed with \( \text{CS}_2 \) and the wash liquor is combined with the filtrate. The carbon disulfide is then evaporated in vacuum. The red evaporation residue is distilled in high vacuum at a bath temperature of 60-65°C. Dark-red crystals separate in a trap cooled with Dry Ice-methanol mixture.

The yield is about 4 g. The autoclave should not be cleaned between runs since the yield is good only if the walls are contaminated with material from a previous \( \text{S}_4\text{N}_2 \) preparation.

**Properties:**

M.p. 23°C; quite unstable; decomposes within a few hours even at 0°C; decomposes explosively to S and N at 100°C; soluble in many organic solvents; insoluble in water; hydrolyzes slowly with water; diamagnetic.

**Reference:**

Disulfur Dinitride

\[ S_2N_2 \]

\[ S_4N_4 = 2S_2N_2 \]

184.3 184.3

The compound is prepared by thermal degradation of \( S_4N_4 \). The reactor is a quartz tube, about 320 mm. long. The diameter of the lower section of the tube is 11 mm., while that of the top half is approximately twice that. As shown in Fig. 167, the upper part of the tube is connected through two condensation traps to a high-vacuum pump; a water-cooled glass finger extends into the upper section of the reactor. All connections are ground glass joints. The narrower, lower section of the reactor is surrounded by two electric furnaces, each heating about half of the section. The lower furnace heats the contents to about 80°C, the upper one to about 300°C.

A small amount (1-2 g.) of \( S_4N_4 \) is placed in the reactor. A 7-cm.-long part of the section heated by the upper furnace is filled with tightly compressed silver wool. The apparatus is evacuated to 0.005 mm. The first condensation trap is then cooled with Dry Ice-methanol and the second trap with liquid nitrogen. The upper furnace is heated to 300°C and only then is the lower one switched on.

The cold finger soon becomes coated with a blue film, and colorless to faintly yellow crystals form in the inlet tube to the first trap. After 6-8 hours, the thermal degradation of \( S_4N_4 \) is complete. The furnaces and the trap coolants are then removed and the apparatus is flushed with dry air or dry \( N_2 \).

Fig. 167. Preparation of disulfur dinitride.
The light-gray crystalline coating in the first trap (which is reddish, with a blue rim, where it extends beyond the cooling zone) is extracted several times with 10-ml. portions of dry ether until only a few dark-blue or shiny metallic crystals remain. The first extract is a deep red because of the byproduct \( S_4N_3 \); since \( S_4N_3 \) dissolves readily, the color of the other extracts is lighter. The combined ether solution is filtered and placed in a conical ground glass flask (which narrows to a point at the bottom) provided with an adapter permitting reverse filtration with exclusion of moisture. The flask is then cooled to \(-80^\circ C\) in a Dry Ice-methanol bath; the white \( S_2N_2 \) crystals precipitate. These are separated from the ether by reverse filtration.

To purify the \( S_2N_2 \) it can be sublimed at room temperature in high vacuum. Beautiful, large, colorless crystals are obtained. The yield, prior to sublimation, is 80%.

It cannot be overemphasized that the preparation and further manipulation of \( S_2N_2 \) must be done very cautiously. Significant polymerization occurs within a short time even at room temperature. The material detonates violently at \( 30^\circ C \), or when under high mechanical pressure.

**PROPERTIES:**

Well-formed, colorless crystals; very volatile; unpleasant iodinelike odor; stable only at low temperature; becomes dark after a short exposure to \( 20^\circ C \); sublimes at \( 10^{-2} \text{ mm} \), even at room temperature; polymerizes readily to \((\text{SN})_X\); in the presence of traces of moisture, about 67% of the \( S_2N_2 \) polymerizes to \((\text{SN})_X\), while 33% dimerizes to \( S_4N_4 \); detonated by shock, friction and temperature above \( 30^\circ C \); soluble in alcohols, yielding yellowish red solutions; readily forms colorless solutions in benzene, ether, carbon tetrachloride, acetone, tetrahydrofuran, dioxane; in the absence of moisture, the colorless solutions are more stable than the solvent-free substance (however, the addition of traces of alkali metals, some NaOH, KCN or \( \text{Na}_2\text{CO}_3 \) causes instantaneous and complete dimerization); crystals are not wetted by water and acids (for this reason, hydrolysis with these solvents occurs very slowly); vigorous reaction with alkali solutions; dissolves rapidly in 2 N NaOH, giving a yellow solution, with larger crystals becoming black and detonating, giving off a pungent gas.

**REFERENCE:**

7. SULFUR, SELENIUM, TELLURIUM

Sulfur Nitride Tetrahydride

\[ \text{S}_4\text{N}_4 + 2[\text{SnCl}_2 \cdot 2\text{H}_2\text{O}] = \text{S}_4(\text{NH})_4 + 2\text{HCl} + 2[\text{Cl} \cdot \text{Sn(OH)}_3 \cdot \text{H}_2\text{O}] \]

\begin{align*}
184.3 & \quad 451.9 & \quad 72.1 & \quad 188.4 & \quad 72.9 & \quad 446.4
\end{align*}

A solution of 10 g. of \( \text{S}_4\text{N}_4 \) in 300 ml. of dry benzene is heated to 80°C in a two-liter flask. A solution of 35 g. of \( \text{SnCl}_2 \cdot 2\text{H}_2\text{O} \) in 80 ml. of methanol containing about 5% water is added all at once. The solution starts to boil and becomes colorless. The precipitate formed is suction-filtered and washed with cold 2N HCl until no Sn remains. It is then washed with alcohol and ether. Further purification is by recrystallization from methanol. The yield is about 6 g.

**PROPERTIES:**

Colorless solid; small, shiny crystals of \( \text{C}_{2\text{h}} \) type; reddens on heating to 80-100°C; m.p. 152°C (provided it is heated very rapidly; otherwise decomposition occurs); not wetted and not dissolved by water; readily soluble in pyridine, slightly soluble in hot acetone and hot alcohol, very slightly soluble in other organic solvents; diamagnetic.

**REFERENCE:**


Heptasulfur Imide

\[ \text{S}_7\text{NH} \]

\[ 36 \text{S}_2\text{Cl}_2 + 98\text{NH}_3 = 6\text{S}_7\text{NH} + 72\text{NH}_4\text{Cl} + 5\text{S}_4\text{N}_4 + 10\text{S} \]

\begin{align*}
1/_{10} & \quad 486.1 & \quad 166.6 & \quad 143.7 & \quad 384.2 & \quad 92.2 & \quad 32.1
\end{align*}

A two-liter, three-neck flask, equipped with a stirrer, a gas inlet tube reaching to the bottom, and a gas outlet tube connected to a KOH drying tube, serves as the reaction vessel. The flask is filled with one liter of dimethylformamide and cooled with an ice-salt mixture, and a fast stream of \( \text{NH}_3 \) is passed through with vigorous stirring. When the solution is saturated with \( \text{NH}_3 \) and the temperature has dropped to −5°C, the gas outlet tube
is briefly removed and 5 ml. of $S_2Cl_2$ is rapidly injected from a pipette without interrupting the inflow of $NH_3$. After the addition of $S_2Cl_2$, the temperature of the reaction mixture increases somewhat; after renewed cooling to $-5^oC$, another 5 ml. of $S_2Cl_2$ is injected into the flask. A total of 100 ml. of $S_2Cl_2$ is added in this manner. Ammonia passage is continued for 15 min., after which stirring is interrupted. The mixture is left to stand for one hour and is then poured into three liters of 1% $HCl$ (precooled to 0°C). Some ice is added. The mixture is stirred, neutralized with 10% $HCl$, and left to stand for 2-3 hours to settle the reaction products ($S$ and $S_2NH$). The supernatant is then decanted; the solid products are washed with water on a filter and dried in a vacuum desiccator over $CaCl_2$. The crude product is shaken with 250 ml. of tetrahydrofuran for one half hour. It is then filtered through a fluted filter paper, and the tetrahydrofuran is removed in aspirator vacuum. The residue is recrystallized from hot methanol. By concentrating the mother liquor, further heptasulfur imide can be obtained. The yield is 16-20 g.

**PROPERTIES:**

M.p. 113.5°C; crystallizes in space group $D_{2h}^2$; $d$ 2.01. Not wetted or dissolved by water; readily soluble in organic solvents; characteristic blue-violet color with acetone when alcoholic alkali hydroxide is added.

**REFERENCES:**


### $a$-Sulfanuric Chloride

$$[OS(N)Cl]_3$$

$$3SO_2Cl_2 + 3SOCl_2 + 12NH_3 = [OS(N)Cl]_3 + 3SO_2 + 9NH_4Cl$$

A mixture of sulfuryl chloride and thionyl chloride (100 ml., mole ratio 2 : 1) is diluted with 100 ml. of low-boiling petroleum ether in a 500-ml., three-neck, ground glass flask equipped with a stirrer, a gas inlet and a drying tube. The flask is cooled in a Dry Ice-methanol bath, and a rapid stream of dry $NH_3$ is passed through for 1.5 hours, while the mixture is continuously stirred.
A yellow slurry is formed. The solvent is removed in vacuum at a bath temperature of about 50°C; the residue is washed with cold water, immediately filtered and dried in a vacuum desiccator. From this water-insoluble reaction mixture, \( \alpha \)-sulfanuric chloride is obtained by sublimation at a bath temperature of 60-80°C and a pressure of 0.05 mm.

The yield is about 1 g.

**Properties:**

White, crystalline substance; not wetted by water; soluble in organic solvents; forms esters with alcohols; hydrolyzes slowly with water; m.p. 144.5°C.

**Reference:**

M. Goehring, Scientia Chimica 9, Ergebnisse und Probleme der Chemie der Schwefelstickstoffverbindungen [Data and Problems in the Chemistry of Sulfur-Nitrogen Compounds], Berlin, 1957, pp. 96, 158.

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**Trisulfur Dinitrogen Dioxide**

\[
\text{S}_3\text{N}_2\text{O}_2
\]

**I.**

\[
\text{S}_4\text{N}_4 + 4\text{SOCl}_2 + 4\text{SO}_2 = 2\text{S}_3\text{N}_2\text{O}_2 + 4\text{SO}_2\text{Cl}_2 + 2\text{S}
\]

\[
\begin{array}{cccccc}
184.3 & 475.9 & 256.2 & 312.4 & 539.9 & 64.1
\end{array}
\]

The reaction vessel is a 100-ml., two-neck, ground glass flask with reflux condenser and gas inlet tube.

Approximately 1 g. of \( \text{S}_4\text{N}_4 \) is reacted with a mixture of equal volumes of \( \text{C}_6\text{H}_6 \) and \( \text{SOCl}_2 \). The quantity of the \( \text{C}_6\text{H}_6-\text{SOCl}_2 \) mixture should be such that a portion of the \( \text{S}_4\text{N}_4 \) remains undissolved. Dry \( \text{SO}_2 \) is then introduced and the flask is heated at 70-75°C for two hours. The solution turns red-brown. The solvent is then evaporated in vacuum at room temperature and the \( \text{S}_3\text{N}_2\text{O}_2 \) is sublimed from the mixture in high vacuum at about 40°C to form large yellow crystals.

The yield is about 0.8 g.

**II.**

Approximately 80 g. of distilled \( \text{SOCl}_2 \) is diluted with 80 g. of dry petroleum ether and cooled to -80°C. A rapid stream of dry \( \text{NH}_3 \) is passed through this solution until the mixture becomes a thick yellow slurry. The reaction must be protected from moisture. The solvent is distilled off in vacuum at room temperature and the dry residue is then transferred into a sublimation vessel; the
product sublimes at a bath temperature of about 40°C and 0.01 mm. The crude product may be recrystallized from dry benzene. The yield is about 6 g.

PROPERTIES:

Well-formed, pale yellow crystals (rhombic, pseudotetragonal); soluble in organic solvents (e.g., benzene, nitrobenzene, heptane, petroleum ether, alcohols; these solutions are stable if the solvent is completely dry); hydrolysis occurs only on prolonged contact with water; immediate hydrolysis in alkaline solution; completely stable when stored in dry air (or dry N₂, dry SO₂) at room temperature; becomes red when heated to 80°C; m.p. 100.7°C (without decomposition); boils on further heating, evolving a yellow vapor which ignites spontaneously in air at about 300°C. When decomposed by moisture, the yellow crystals first turn red, then black and finally white (the odor of SO₂ is apparent).

REFERENCE:


Trisulfur Dinitrogen Pentoxide

\[ S₃N₄ + 6SO₂ \rightarrow 2S₂N₂O₅ + 4SO₂ \]

The reactor is a 4-cm.-diameter tube with a capacity of 200 ml. A water-cooled cold finger, extending through about 4/5 of the tube length, is inserted through a ground glass connection. A flask filled with oleum, a vacuum line, and a pressure release valve (protected with an H₂SO₄ drying tube) are connected to the reaction tube via stopcocks.

A 5-g. quantity of S₄N₄ is placed in the tube. The cold finger is then cooled with running water and the tube is evacuated to about 15 mm. The stopcock to the flask containing the oleum is now opened; the flask is evacuated and heated until SO₃ distills out. It condenses on the cold finger and then drips onto the sulfur nitride below. Immediately after the start of the reaction, the reactor is cooled with ice water. The S₄N₄ first turns black-brown and SO₂ is evolved. Later, when the substance reverts to light yellow and is covered with some liquid SO₃, the stopcock to
The oleum flask is closed and the stopcock to the pressure release valve is opened so that the $SO_2$ may escape. The cooling bath is now removed and the mixture allowed to stand at room temperature for about six hours. The excess $SO_3$ is distilled back into the oleum flask by opening the stopcock to this flask, evacuating the reaction vessel to 15 mm., cooling the oleum flask to 0°C, and heating the reaction tube to 30°C. If the reactor is then heated briefly to 60°C, even the last traces of $SO_3$ can be removed. Finally, the stopcock to the oleum flask is closed again, the apparatus is evacuated to 1 mm., and the reactor is heated to 70-80°C. Most of the $S_3N_2O_5$ product sublimes onto the cold finger.

The yield is about 5 g.

**Properties:**

Well-formed, almost colorless crystals, which can be sublimed in vacuum; completely stable when stored dry; readily soluble in organic solvents (e.g., nitrobenzene) without decomposition; vigorous reaction with traces of moisture. The compound is characterized most easily by its powder pattern.

**Reference:**


**Selenium**

Se

**Very Pure Selenium**

Commercial selenium frequently contains some sulfur as well as small amounts of tellurium and iron. To remove these, it is oxidized to $SeO_2$; the latter is purified by repeated sublimation and is then reduced again to elemental selenium.

The oxidation of Se to $SeO_2$ should be carried out according to the procedure given under $SeO_2$, with particular attention to the purity of all reagents used. The subsequent resublimation is also carried out in the manner described. The final sublimate, consisting of loose, colorless crystals, is dissolved in water, re-filtered (if needed), and then reduced in a stirred flask placed on the water bath by the gradual addition of 10% hydrazinium hydroxide solution. The Se precipitates as a red powder which, when heated,
soon coagulates to form a grayish-black precipitate. An excess of the reducing agent should be avoided as it dissolves Se, forming red polyselenides. (These may be decomposed by the addition of hydrochloric acid.) The Se is filtered off and washed several times with hot water until the filtrate ceases to give a blue color on addition of KI-starch solution. The entire purification procedure is then repeated. The dark powder obtained after the second reduction is thoroughly washed, dried at 170°C, and, if desired, distilled in a stream of N₂ to remove the last traces of adsorbed moisture (a quartz apparatus should be used).

REFERENCES:


MODIFICATIONS OF SELENIUM

a) AMORPHOUS SELENIUM

Amorphous selenium is formed by reduction of Se compounds at moderate temperatures. Depending on the state of aggregation, it may be red to black in color.

To prepare amorphous red Se, SO₂ is passed at 15 to 20°C through an aqueous H₂SeO₃ solution strongly acidified with hydrochloric acid. The finely powdered Se precipitate is carefully washed free of Cl⁻ and SO₄²⁻ ions and dried in a vacuum desiccator over CaCl₂.

Dark, amorphous Se is obtained by treating red Se with boiling water. It is also formed by reduction of heated selenous acid with hydrazinium hydroxide (see Very Pure Selenium above). The grayish-black powder is thoroughly washed with warm water and dried in vacuum over CaCl₂.

Both forms of amorphous Se are stable at room temperature.

b) AMORPHOUS, VITREOUS SELENIUM

Vitreous Se is formed on rapid cooling of molten Se.

Solid selenium of any available modification is melted and poured in a thin stream into cold water. Strands of brittle, vitreous Se are obtained. Thin layers of this material are translucent and red, while thick layers are grayish black. The substance can be stored for a long time at room temperature.

c) MONOCLINIC α-SELENIUM AND β-SELENIUM

The two monoclinic modifications are formed together when amorphous Se is treated with CS₂.
A few grams of amorphous red Se are refluxed for two hours in one liter of CS₂. The orange, slightly green-tinted solution is allowed to evaporate slowly at room temperature in a vessel protected from dust. Large red crystals of α-Se along with smaller, dark prisms of β-Se are formed. They can be separated by sorting under the microscope. Both forms are quite stable at room temperature.

d) HEXAGONAL SELENIUM

Metallic, hexagonal selenium is formed when any one of the other selenium modifications is heated above 130°C.

Monoclinic Se, vitreous Se or powdered amorphous Se is vacuum heated for some time (10 hours or more) at 200°C until complete conversion to the metallic form has occurred. The product is lead gray, finely crystalline and granular.

A highly ordered Se solid, in which no lattice imperfections can be detected by x ray analysis, is obtained only after annealing for several days at 200 to 218°C. The crystallization of Se can be catalyzed by various substances.

For methods of preparing single crystals up to 10 mm. long and 0.5 mm. in diameter, see the cited literature.

e) COLLOIDAL SELENIUM

Stable, essentially monodispersed Se sols are obtained by reduction of selenous acid with hydrazinium hydroxide. A mixture of 90 ml. of distilled H₂O and 5 ml. of 1.5M N₂H₅OH solution is heated, and 4 ml. of pure H₂SeO₃ solution (0.1M) is added when the temperature reaches 100°C. When the mixture turns dark yellow, 1 ml. of the same H₂SeO₃ solution is added. The flame is then removed; the solution is cooled for about 10 minutes and diluted to 400 ml. with distilled H₂O. When stored in the dark, the sol is stable for a fairly long period. On the other hand, it flocculates quantitatively in a short time on exposure to direct sunlight. The particle count is 3-4·10¹⁰/ml. If the 5 ml. of H₂SeO₃ solution is added all at once to a vigorously boiling solution of reducing agent, a greater number of particles (10-12·10¹⁰/ml., diameter about 75 mµ) is obtained. The sols may be freed of the electrolyte by dialyzing.

REFERENCES:


c) W. Muthmann, Z. Kristallogr. 17, 336 (1890); F. Halla, F. X. Bosch and E. Mehl, Z. phys. Chem. (B) 11, 455 (1931); H. P. Klug, Z. Kristallogr. 88, 130 (1934).


Hydrogen Selenide

$\text{H}_2\text{Se}$

Hydrogen selenide is even more poisonous than $\text{H}_2\text{S}$. It very strongly attacks the mucous membranes of the eyes, nose and throat ("selenium fever"). The preparation must therefore be carried out under a very good hood, using a carefully sealed apparatus with the outlets directly connected to the stack.

\[ \text{Al}_2\text{Se}_3 + 6\text{H}_2\text{O} = 3\text{H}_2\text{Se} + 2\text{Al(OH)}_3 \]

290.82 108.10 242.93

The reactor is a dry 500-ml. ground glass flask equipped with a separatory funnel and gas inlet and outlet tubes. The outlet tube is connected to the drying and condensation apparatus; the latter consists of two U tubes, containing CaCl$_2$ and P$_2$O$_5$-glass wool, as well as two glass condensation traps cooled to $-78^\circ$C. The flask is filled with pure dry Al$_2$Se$_3$ (for preparation see section on Aluminum) and the apparatus is flushed for 15-20 minutes with oxygen-free, dry N$_2$ until all air is displaced. While a slow stream of N$_2$ is passed through, freshly distilled cold water is added slowly from the separatory funnel. The addition must be regulated so that the reaction is not too violent and the flask heats up only very slightly. A little dilute hydrochloric acid is added toward the end, when the gas evolution subsides. The condensate collected in the traps is 100% H$_2$Se, provided all starting materials used in the preparation of Al$_2$Se$_3$ were pure. The yield is about 85%.

Hydrogen selenide can be stored in liquid form at low temperatures or as a vapor in sealed glass flasks.

\[ \text{H}_2 + \text{Se} = \text{H}_2\text{Se} \]

2.02 78.96 80.98

A mixture of oxygen-free, dry H$_2$ and pure selenium vapor is passed through a combustion tube filled with pumice fragments and
heated to 350-400°C. For the arrangement of the apparatus and the procedure, see the analogous synthesis of $\text{H}_2\text{S}$ (p. 344) as well as the original literature. After passing through traps cooled to $-20^\circ\text{C}$ and $-40^\circ\text{C}$, the $\text{H}_2\text{S}$ is frozen out with liquid nitrogen; after another distillation in high vacuum, it is very pure.

**PROPERTIES:**

Colorless gas with an unpleasant odor "reminiscent of rotten radishes"; very poisonous. Decomposed by dust, rubber and, in the presence of moisture, also by atmospheric oxygen, with separation of selenium. For this reason, rubber connections are to be avoided. M.p. $-65^\circ\text{C}$, b.p. $-42^\circ\text{C}$, crit. t. $+141^\circ\text{C}$, crit. p. 91 atm. d. (liq. $-42^\circ\text{C}$) 2.12, d. (solid $-170^\circ\text{C}$) 2.45; weight per liter 3,6643 g.

More soluble in water than $\text{H}_2\text{S}$; solubility at 760 mm. in 1 vol. part $\text{H}_2\text{O}$ ($4^\circ\text{C}$) 3.77; ($13.2^\circ\text{C}$) 3.31; ($22.5^\circ\text{C}$) 2.70 vol. parts $\text{H}_2\text{Se}$. In air, the initially colorless solution rapidly becomes cloudy, with separation of red Se.

The Se atoms in crystalline $\text{H}_2\text{Se}$ form a cubic face-centered lattice; probably structure type C1 or C2.

**REFERENCES:**


**Sodium Hydrogen Selenide**

$\text{NaHSe}$

$\text{C}_2\text{H}_5\text{ONa} + \text{H}_2\text{Se} = \text{NaHSe} + \text{C}_2\text{H}_5\text{OH}$

Because of the instability of NaHSe and $\text{H}_2\text{Se}$ in moist air, the preparation must be carried out in the closed apparatus shown in Fig. 168.
Oxygen-free, dry N\textsubscript{2} is introduced at \textit{a}, and the apparatus is carefully purged until all air is displaced. Then a small tube, containing highly pure, vacuum-distilled Na (see section on Alkali Metals), the tip of which has been broken just prior to insertion, is pushed with the open end down into attachment \textit{C}, and the latter is rapidly closed off with a rubber stopper. After evacuating through 2 with stopcocks 1, 3 and 4 closed, the metal is melted in high vacuum and allowed to flow into reaction vessel \textit{A}. Capillary \textit{k\textsubscript{1}} is then fused to form a seal. Section \textit{A} is then cooled with an ice-salt mixture, and carefully dehydrated alcohol is added from \textit{D} in small portions until an alcoholic ethoxide solution is formed. When the

![Diagram of the preparation of sodium hydrogen selenide](image)

**Fig. 168.** Preparation of sodium hydrogen selenide.

reaction is complete, \textit{A} is warmed again to room temperature. Then a mixture of pure dry H\textsubscript{2} and H\textsubscript{2}Se is allowed to enter at \textit{a} with the three-way stopcock 1 turned so that the gas escapes at \textit{d} and thus flushes the stopcock holes free of air; only then is it introduced into the apparatus by turning stopcock 1. The solution heats up considerably during the reaction. At first the gas is allowed to escape at \textit{d}; when section \textit{B} is sufficiently filled with H\textsubscript{2}Se, the gas is allowed to escape at \textit{2}. As soon as the reaction subsides, the H\textsubscript{2} inflow is stopped and pure H\textsubscript{2}Se is introduced. The end of the reaction is recognized by the absence of vapor mists and cooling of vessel \textit{A}. Stopcock 2 is then closed and stopcock 3 opened, the apparatus is tilted, and the NaHSe solution is forced to flow toward \textit{B} under hydrogen pressure. Capillary \textit{k\textsubscript{2}} is then fused shut. The
alcohol is evacuated with an aspirator through c. Finally, high vacuum is applied, and the remaining fine, white crystals of NaHSe are dried at about 50°C. The product is then analytically pure.

PROPERTIES:

White crystals; very unstable in moist air, separating Se and forming polyselenides.
Rhombohedrally distorted NaCl structure.

REFERENCE:

_Sodium Selenide, Potassium Selenide_

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<td>Na</td>
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<td>78.19</td>
<td>78.96</td>
<td>157.15</td>
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The reaction is carried out in liquid NH3. For apparatus and procedure, see K2S (p. 360). The directions given there may be applied without change. The white Na2Se or K2Se is analytically pure.

PROPERTIES:

White, fine, hygroscopic crystals; rapidly turns red in moist air because of Se separation and formation of polyselenides.
Na2Se: m.p. > 875°C, d 2.58.
K2Se: On heating, initially brown, then black, d 2.29 (by x-ray). Both compounds are soluble in water; red Se separates rapidly on contact with air.
Crystallizes in Cl structure type.

REFERENCE:

_Sodium Diselenide_

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<tr>
<td>Na</td>
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<td>Na2Se</td>
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<tr>
<td>124.95</td>
<td>78.96</td>
<td>203.91</td>
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About 2.5 g. of Na2Se and the stoichiometric amount of Se are placed in a small glass tube in a vigorous oxygen-free stream of
dry N₂. The tube is sealed off in high vacuum and then heated in an electric furnace to 500°C until a homogeneous melt is formed (about 45 min.). The gray-black, very hard mass that forms on cooling is Na₂Se₂.

PROPERTIES:

Dull gray-black, microcrystalline substance; very hygroscopic; decomposes in moist air, turning red.

M.p. about 495°C.

Readily soluble in water, forming a red solution which decomposes rapidly on contact with air, separating selenium.

REFERENCES:


Diselenium Dichloride
Se₂Cl₂

I. \[ 3\text{Se} + \text{SeO}_2 + 4\text{HCl} = 2\text{Se}_2\text{Cl}_2 + 2\text{H}_2\text{O} \]

\[
\begin{array}{ccccc}
236.88 & 110.96 & 145.86 & 457.87 \\
\end{array}
\]

A solution of 115 g. of freshly sublimed SeO₂ in 500 ml. of concentrated hydrochloric acid (36-37%) is prepared in a wide-neck flask, and 235 g. of pure Se is added. Then concentrated H₂SO₄ is added in drops from a separatory funnel until HCl evolution ceases. The mixture is cooled. The Se₂Cl₂, which settles at the bottom as a red layer, can then be removed in the separatory funnel. To purify the product, it is either washed several times with concentrated H₂SO₄, or it is dissolved in fuming sulfuric acid and reprecipitated with HCl. Any adhering H₂SO₄ is removed by treating with anhydrous BaCl₂ and subsequent filtering through fritted glass. The filtration must be protected from moisture. The yield of red-brown Se₂Cl₂ is about 90%.

II. \[ 2\text{Se} + 2\text{SO}_3 + 3\text{HCl} = \text{Se}_2\text{Cl}_2 + \text{H}_2\text{SO}_3 + \text{SO}_2(\text{OH})\text{Cl} \]

\[
\begin{array}{ccccc}
157.92 & 160.13 & 109.40 & 228.83 & 82.08 & 116.54 \\
\end{array}
\]

A distillation flask is filled with 300 g. of 30% oleum, and 100 g. of finely powdered Se is added with constant stirring. The flask
SULFUR, SELENIUM, TELLURIUM

is equipped with a gas inlet tube extending to the bottom and is connected to a downward condenser, connected to a receiver. From the receiver, a gas outlet tube leads (through an H₂SO₄ wash bottle) directly to the stack of the hood. A fast stream of dry HCl (p. 280) is bubbled through the reaction mixture, which is carefully heated until Se just begins to volatilize. After a short time, crude Se₂Cl₂ begins to distill into the receiver at a uniform rate. The distillation rate is adjusted so that about 130 g. distills in two hours. The crude product is shaken several times with small amounts of fuming sulfuric acid until it no longer turns green (SeSO₃), then allowed to stand for some time over anhydrous BaCl₂, and finally filtered through a fritted glass filter protected from access of moisture.

Stored in sealed glass ampoules.

SYNONYMS:

Older names: selenium monochloride and selenous chloride.

PROPERTIES:

Dark red, oily liquid with a brown tint; odor similar to S₂Cl₂; sensitive to moisture. M.p. −85°C, b.p. (733 mm.) 127°C with partial decomposition into Se and SeCl₄; cannot be distilled without decomposing, even at reduced pressure. d₄⁰ 2.77.

Slowly hydrolyzed by water, forming H₂SeO₄, HCl and Se. Dissolves without decomposition in CS₂ and CHCl₃.

REFERENCES:


**Selenium Tetrachloride**

\[ \text{SeCl}_4 \]

\[ \text{Se} + 2 \text{Cl}_2 = \text{SeCl}_4 \]

\[ \text{78.96} \quad \text{141.83} \quad \text{220.79} \]

I. DIRECT CHLORINATION OF SOLID Se:

A 1- to 15-cm. section of a 1.5-m.-long combustion tube is filled with pure granulated Se (free of Te). The filled section starts at a distance of 10 cm. from one end. The tube is closed at both ends.
with one-hole rubber stoppers holding gas inlet and outlet tubes. The inlet is at the end close to the Se layer. The outlet tube is connected, through a CaCl$_2$ drying tube, to the hood stack. The middle and rear sections of the tube are cooled with strips of wet filter paper, and pure, dry chlorine gas is introduced at room temperature. The reaction begins immediately, with absorption of Cl$_2$ and heating of the selenium layer. Toward the end of the reaction, the selenium must be heated somewhat with a multiple-flame burner. The SeCl$_4$ deposits in the colder section of the tube. It is then sublimed several times (in the direction of the tube rear) in a fast stream of Cl$_2$ in order to remove small amounts of SeOCl$_3$. The pure product is loosened from the glass wall by light tapping, with heating if necessary. It is then quickly shaken out of the reactor and sealed in ampoules. The yield is about 90%.


II. CHLORINATION OF Se IN AN INERT SOLVENT:

Pure Se is suspended in CCl$_4$ in a round-bottom flask provided with a gas inlet and outlet. Dry Cl$_2$ is then introduced. The Se soon dissolves and the solution turns brown (formation of Se$_3$Cl$_2$); after some time, SeCl$_4$ separates as a yellow-white powder. It is rapidly filtered by suction (the filtration must be protected from moisture) on a fritted glass filter, washed with a small amount of CCl$_4$, and dried in a vacuum desiccator over silica gel.

PROPERTIES:

White to faintly yellow crystalline substance; decomposes in moist air. On heating, sublimes without melting; the change in the color of the vapor from yellow to red with increasing temperature indicates increasing dissociation; subl. p. about 196$^\circ$C. Melts in a closed tube at about 305$^\circ$C to form a dark red liquid, d 3.80.

With water, it hydrolyzes exothermically to form H$_2$SeO$_3$ and HCl.

REFERENCES:


Hexachloroselenium Salts

The stock solution for the preparations is prepared by dissolving 5.5 g. of SeO₂ in hydrochloric acid; alternatively, 4 g. of finely powdered gray Se is added to 50 ml of concentrated hydrochloric acid, and Cl₂ is passed through with frequent swirling or stirring until the initially dark brown sludge of SeCl₂ is completely dissolved and the solution is brownish-yellow.

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

\[
\text{SeCl}_4 + 2\text{NH}_4\text{Cl} = (\text{NH}_4)_2\text{SeCl}_6
\]

For example, 5 ml. of an aqueous solution of 0.55 g. of NH₄Cl (~10 mmoles) is added to 5 ml of the SeCl₄ solution containing 5 mmoles of SeCl₄, and HCl gas is passed through at 0°C with frequent shaking. The \([\text{SeCl}_4]^2\text{−}\) concentration increases with increasing HCl concentration and determines the point of precipitation. Precipitation of the deep yellow complex salt, which soon commences, is nearly quantitative if the solution is saturated with HCl. The solution is then colorless.

\[
\text{K}_2\text{SeCl}_6
\]

\[
\text{SeCl}_4 + 2\text{KCl} = \text{K}_2\text{SeCl}_6
\]

For example, 15 ml of a concentrated hydrochloric acid solution of 0.75 g. of KCl (~10 mmoles) is added to 5 ml of the SeCl₄ solution and the complex is precipitated as discussed under (NH₄)₂SeCl₆.

To isolate these moisture-sensitive complexes, the apparatus described for the preparation of hexachlorotitanium salts (compare section on Titanium) can be used.

Tl₂SeCl₆ cannot be made by reaction in hydrochloric acid solution, since the Se⁴⁺ is reduced to elemental Se.

Rb₂SeCl₆ and Cs₂SeCl₆ are analogously obtained from concentrated hydrochloric acid solutions even at room temperature.

**PROPERTIES:**

[(NH₄)₂SeCl₆ and K₂SeCl₆]: Yellow octahedra with an average diameter of 0.03 mm. Very sensitive to moisture; when moistened with hydrochloric acid, complete decomposition and loss of color occur in air in about 10 minutes. Very readily soluble in water with complete hydrolysis to selenic and hydrochloric acids; nearly
insoluble in concentrated hydrochloric acid. The complex salt reprecipitates on passage of HCl through a not too dilute aqueous solution at 0°C.

Crystal structure: $K_2PtCl_6$ type.

REFERENCES:

**Diselenium Dibromide**

$Se_2Br_2$

I. $2Se + Br_2 = Se_2Br_2$

157.92 159.83 317.75

A round-bottom flask, equipped with a separatory funnel and gas outlet tube connected to a $P_2O_5$ drying tube, is filled with a suspension of 20 g. of pure powdered Se in 50 ml. of dry $CS_2$; 20 g. of pure $Br_2$ is then slowly added from the separatory funnel. If the flask is occasionally shaken, the reaction is soon complete. A reddish-brown solution is formed, from which the $CS_2$ is evaporated in vacuum as rapidly as possible. The product is deep-red, pure $Se_2Br_2$.

II. $3Se + SeO_2 + 4HBr = 2Se_2Br_2 + 2H_2O$

236.88 110.96 323.70 635.50

A wide-neck flask is filled with 400 ml. of $H_2O$ and this is saturated at 0°C with $SO_2$. While the $SO_2$ passage is continued, 135 ml. of $Br_2$ is gradually added from a separatory funnel. When the $Br_2$ is completely consumed and the solution becomes colorless, 115 g. of $SeO_2$ and then 235 g. of Se are added at room temperature. About one liter of concentrated $H_2SO_4$ is then added, the reaction mixture is allowed to cool, and the dark red, oily layer is removed in a separatory funnel. The product is purified by repeated washing with concentrated $H_2SO_4$. The yield of $Se_2Br_2$ is about 90%.

SYNONYMS:

Older names are selenium monobromide and selenous bromide.

PROPERTIES:

Dark red, almost black, oily liquid with an unpleasant odor; hygroscopic; rapidly liberates $Br_2$ in air, simultaneously separating
Se. Partially decomposed on heating; first, some Br$_2$ escapes, then some SeBr$_4$ sublimes, and between 225 and 230°C a part of the Se$_2$Br$_2$ boils without decomposition, leaving a residue of Se.

d (15°C) 3.604.

In water, Se$_2$Br$_2$ sinks to the bottom in oily drops and gradually decomposes into Se, SeO$_2$ and HBr; soluble in CS$_2$ and CHCl$_3$.

REFERENCES:


Selenium Tetrabromide

SeBr$_4$

Se + 2 Br$_2$ = SeBr$_4$

78.96 319.66 398.62

The reaction is carried out in a round-bottom flask equipped with a separatory funnel and gas outlet tube connected to a P$_2$O$_5$-glass wool drying tube. Pure Br$_2$ (100 g.) is allowed to flow slowly into a suspension of 20 g. of pure powdered Se in 50 ml. of dry CS$_2$. Finely crystalline yellow SeBr$_4$ separates. When the addition is complete, a gas inlet tube is substituted for the separatory funnel and the CS$_2$ and excess Br$_2$ are driven off with a dry air stream. The residual SeBr$_4$ is rapidly transferred into a tightly sealed vessel.

PROPERTIES:

Fine, ochre-yellow crystals with an unpleasant odor reminiscent of S$_2$Cl$_2$; hygroscopic; decomposes in moist air to Br$_2$, Se$_2$Br$_3$ and reddish-brown Se. On heating, Br$_2$ evolves. Between 75°C and 80°C, a mixture of SeBr$_4$ and Se$_2$Br$_2$ sublimes, forming black, shiny crystals.

With water, SeBr$_4$ forms a clear solution of H$_2$SeO$_3$ and HBr.

REFERENCES:

See also R. Schneider, Pogg. Ann. 129, 450 (1866).
Selenium Dioxide

\[ \text{SeO}_2 \]

I. \[ \text{Se} + \text{O}_2 = \text{SeO}_2 \]

A large porcelain boat containing 60 to 75 g. of Se is pushed into the front end of a Pyrex glass tube (50-70 cm. long, 4-5 cm. in diameter); the tube is closed with a one-hole rubber stopper, and a fast \( \text{O}_2 \) stream, which has passed successively through a wash bottle containing fuming \( \text{HNO}_3 \) and a drying tube containing \( \text{P}_2\text{O}_5 \)-glass wool, is introduced. A two-liter, two-neck glass bulb is mounted over the rear end of the tube. The front end of the boat is heated with a fishtail burner so that the Se melts and, shortly afterward, ignites, forming a long, luminous blue flame. The \( \text{SeO}_2 \) deposits to the rear of the tube, behind the boat. The \( \text{O}_2 \) stream must be very fast or elemental Se will also distill off and darken the \( \text{SeO}_2 \). To avoid plugging of the tube, the sublimate is driven forward from time to time by means of a second burner. Traces of \( \text{SeO}_2 \), which are carried along in the gas stream, are retained in the glass bulb. When all the Se has burned (about 1.25 hours) and only impurities remain in the boat, the product is repeatedly sublimed in the same tube in a pure \( \text{O}_2 \) stream until it is snow white; this removes small amounts of Se and nitrogen oxide impurities. The \( \text{SeO}_2 \) is then very pure and completely dry. The yield is about 90%, based on 100% pure Se.

Pure \( \text{SeO}_2 \) can be stored without decomposition only in carefully cleaned, well-sealed glass containers; even dust reduces it partially to Se. Very hygroscopic.

II. \[ \text{Se} + 4 \text{HNO}_3 = \text{H}_2\text{SeO}_3 + 4 \text{NO}_2 + \text{H}_2\text{O} \]

\[ \text{H}_2\text{SeO}_3 = \text{SeO}_2 + \text{H}_2\text{O} \]

Pure Se is slowly added to pure, concentrated, heated nitric acid, the solution is evaporated to dryness on a sand bath, and the residue is heated until sublimation begins. It is then absorbed in water and, to remove all \( \text{H}_2\text{SeO}_4 \) present, \( \text{Ba(OH)}_2 \) solution is added dropwise until the precipitate ceases to form. The solution is filtered and reevaporated to dryness while stirring. The crude product is powdered and repeatedly sublimed. For very pure material the compound is sublimed in pure \( \text{O}_2 \) as in method I. For many purposes, however, it is sufficient to sublime it two or three times from a porcelain dish into an inverted beaker or an inverted funnel.
containing a glass wool plug in the stem. The SeO$_2$ obtained in this manner, in contrast to that obtained in the dry oxidation process I, is not completely anhydrous, but the moisture can be removed by subsequent heating for 3–4 hours in an air stream at 150°C.

**PROPERTIES:**

White, crystalline substance; poisonous; hygroscopic, forms \( \text{H}_2\text{SeO}_3 \) with moisture; readily discolors in the presence of small amounts of reducing materials (e.g., dust), separating free Se. Sublimes at 315°C, forming shiny needles. Can be melted without decomposition in a closed tube at somewhat higher temperature, d 3.95.

Readily soluble in water (at 20°C about 70 wt.% SeO$_2$) and alcohol.

Crystallizes in C 47 structure type.

**REFERENCES:**


**Selenium Oxychloride**

\[ \text{SeO}_2 + 2 \text{HCl} = \text{SeO}_2 \cdot 2 \text{HCl} \]

110.96 72.93 183.89

\[ \text{SeO}_2 \cdot 2 \text{HCl} + \text{H}_2\text{SO}_4 = \text{SeOCl}_2 + \text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O} \]

183.89 98.08 165.87

Carefully dried HCl is introduced into a weighed, 150-ml. round-bottom flask containing 50 g. of SeO$_2$ until all the SeO$_2$ dissolves, forming SeO$_2$·2HCl (theoretical weight increase, 33 g.). The flask must be occasionally shaken and protected from moisture. Since this reaction may be violent, it is best to insert an empty 500-ml. flask between the reaction flask and the wash bottles at the inlet (which are filled with concentrated H$_2$SO$_4$ in order to dry the HCl gas). To dehydrate the SeO$_2$·2HCl, it is treated in the reaction flask for 10 minutes with 10 ml. of concentrated H$_2$SO$_4$ while being slowly warmed to 50°C and constantly shaken. The partially dehydrated SeO$_2$·2HCl settles as the lower layer; it is then separated in a 100-ml. separatory funnel. The dehydration of the separated layer is repeated under the same conditions, each time
with 5 ml. of concentrated H$_2$SO$_4$, until no further separation takes place. It should be noted that too large an excess of H$_2$SO$_4$, as well as insufficient dehydration, results in low yields and difficulties in the subsequent distillation.

Before the distillation, the cherry-red product is chlorinated until its color becomes straw yellow. In this process, the SeCl$_2$ is converted to SeCl$_4$, which in turn reacts with SeO$_2$ to form SeOCl$_2$. The chlorinated product is distilled twice in aspirator vacuum, using a boiling capillary. The distillation must be protected from moisture; the first milliliter is always discarded. The distillation is continued until fairly large quantities of SeO$_2$ accumulate, causing heavy bumping. If the product ceases to be straw yellow before the second distillation, additional chlorine may have to be introduced.

Caution: All safety rules must be observed during distillation (safety goggles!) since violent decomposition may occur if the SeOCl$_2$ was incompletely dehydrated. For this reason, it is always necessary to determine, immediately prior to the distillation, whether the SeOCl$_2$ is completely dehydrated. (When heated in concentrated H$_2$SO$_4$, SeOCl$_2$ must form a clear solution.)

The yield is about 50 g., i.e., 68% based on SeO$_2$ input. Since the pure product is very hygroscopic, it is transferred in the absence of moisture and stored in glass ampoules sealed off with a torch.

SYNONYM:

Selenyl chloride.

PROPERTIES:

Straw yellow liquid which fumes in moist air; hygroscopic; corrosive to skin. M.p. 11°C, b.p. 179°C with slight decomposition, d (20°C) 2.43. Hydrolyzes in water to form H$_2$SeO$_3$ and HCl; completely miscible with CCl$_4$, CHCl$_3$, CS$_2$, benzene and toluene.

Because of its dissolving ability, SeOCl$_2$ is occasionally used as a solvent for many substances.

REFERENCE:


Selenous Acid (anhydrous)

H$_2$SeO$_3$

SeO$_2$ + H$_2$O = H$_2$SeO$_3$

110.96 18.02 128.98

Pure SeO$_2$ (p. 428) is placed in a porcelain dish and dissolved in a small amount of water. The solution is concentrated on a
water bath with careful exclusion of dust particles (danger of reduc-
tion to Se) until crystallization starts. After cooling, the
separated $\text{H}_2\text{SeO}_3$ is filtered by suction through a fritted glass
filter and recrystallized from water. The pure product is pressed
between filter papers and dried for several days in a vacuum
desiccator over KOH. On prolonged standing over concentrated
$\text{H}_2\text{SO}_4$ or $\text{P}_2\text{O}_5$, further dehydration to $\text{SeO}_2$ occurs.

PROPERTIES:

Colorless, prismatic crystals, which lose water in dry air, forming $\text{SeO}_2$, but gradually liquefy in the presence of moisture;
poisonous; easily reduced (even by dust) to Se. Melts at about
70°C to form a light yellow solution of $\text{SeO}_2$ in $\text{H}_2\text{O}$. $\text{d}^\text{15} = 3.00$. Very readily soluble in water.
Crystal form: hexagonal.

REFERENCES:


Sodium Selenite

$\text{Na}_2\text{SeO}_3 \cdot 5\text{H}_2\text{O}$

$$\text{H}_2\text{SeO}_3 + 2\text{NaOH} = \text{Na}_2\text{SeO}_3 + 2\text{H}_2\text{O}$$

(5 $\text{H}_2\text{O})$
128.98 80.01 203.04

A concentrated aqueous solution of selenous acid is mixed with
the stoichiometric quantity of carbonate-free sodium hydroxide
solution. The mixture is concentrated at room temperature in
vacuum over CaCl$_2$, and crystallization is induced by occasionally
rubbing the vessel wall with a glass rod. The salt tends to form
supersaturated solutions and then precipitates from these in
microscopically small needles, which agglomerate into bundles.
If these are used for seeding a saturated solution and the latter
is allowed to evaporate further, transparent prisms up to 3 mm.
long may be obtained. The crystals are filtered by suction through
a fritted glass filter and dried on clay in a desiccator (do not place
drying agents in the desiccator). The $\text{Na}_2\text{SeO}_3 \cdot 5\text{H}_2\text{O}$ thus obtained
is analytically pure.
PROPERTIES:

White crystals, needle-shaped to prismatic; stable in moist air; in dry air, loses water at the surface; poisonous; sensitive to reducing agents. On heating to 40°C, converts to the anhydrous salt.

Very readily soluble in water; 100 g. of solution contains about 68 g. of \( \text{Na}_2\text{SeO}_3 \cdot 5\text{H}_2\text{O} \) at 20°C.

REFERENCE:


**Selenic Acid**

\[
\text{H}_2\text{SeO}_4
\]

\[
\text{SeO}_2 + \text{H}_2\text{O}_2 = \text{H}_2\text{SeO}_4
\]

110.96 34.02 144.98

The oxidation is carried out in aqueous solution so that dilute selenic acid solution is obtained first; this may be concentrated to the anhydrous acid by evaporation.

A solution of 150 g. of pure \( \text{SeO}_2 \) (p. 428) in 100 ml. of distilled water is prepared in a one-liter ground glass flask with a side gas inlet tube extending to the bottom. Then 500 g. of 30% \( \text{H}_2\text{O}_2 \) (Perhydrol) is slowly introduced. The mixture is refluxed for 12 hours while \( \text{O}_2 \) is passed through. The selenic acid solution formed contains traces of \( \text{H}_2\text{SeO}_3 \) as the only impurity.

To concentrate the solution, most of the water is distilled off in a slow stream of \( \text{P}_2\text{O}_5 \)-dried air and aspirator vacuum until the temperature of the solution reaches 150°C (about four hours are required for this). The acid concentration is then 85-90%. For further dehydration it is distilled at 1-2 mm.; the temperature in the flask should not exceed 160°C, or decomposition to \( \text{H}_2\text{SeO}_3 \) occurs. To avoid local overheating at the flask walls above the liquid level, it is best to heat on a small hotplate and not in an oil bath. When no further \( \text{H}_2\text{O} \) flows into the condenser and the receiver, the oily liquid is transferred to a flat dish and seeded at 10-15°C with a small amount of solid \( \text{H}_2\text{SeO}_4 \). The latter is obtained by cooling a few milliliters of the solution in a Dry Ice bath. To crystallize the solution, it is allowed to stand in a desiccator over \( \text{P}_2\text{O}_5 \). The more complete the dehydration during distillation, the more readily will the acid solidify. The crystals are completely dehydrated by standing in a \( \text{P}_2\text{O}_5 \)-dried air stream at 5 mm, for several days. The yield is about 190 g. of 97-98% \( \text{H}_2\text{SeO}_4 \) containing about 2-3% \( \text{H}_2\text{SeO}_3 \).
7. SULFUR, SELENIUM, TELLURIUM

PROPERTIES:

Anhydrous $\text{H}_2\text{SeO}_4$ forms colorless prismatic or needle-shaped crystals; extremely hygroscopic. M.p. $58^\circ\text{C}$; the melt tends to supercool. On heating, decomposes into $\text{SeO}_2$, $\text{O}_2$ and $\text{H}_2\text{O}$. 

$d$ (solid) ($15^\circ\text{C}$) 2.95, $d$ (liq.) ($15^\circ\text{C}$, supercooled) 2.60. Readily soluble in water.

REFERENCES:


Sodium Selenate

$\text{Na}_2\text{SeO}_4$

$\text{H}_2\text{SeO}_4 + \text{Na}_2\text{CO}_3 = \text{Na}_2\text{SeO}_4 + \text{CO}_2 + \text{H}_2\text{O}$

$144.98 \quad 106.00 \quad 188.95$

About 210 g. of 85-90% selenic acid solution (p. 432) is used to neutralize 125 g. of C.P. $\text{Na}_2\text{CO}_3$. After filtering, the salt solution is evaporated (with heating) until a significant quantity of sediment is formed. If the solution acquires a slight reddish or brownish color due to colloidal Se, it is rediluted with $\text{H}_2\text{O}$, boiled and filtered after standing for 1-2 days. It must then be reconcentrated. The $\text{Na}_2\text{SeO}_4$ is suction-filtered from the mother liquor, which is kept as warm as possible (the temperature of the solution must not fall below $45^\circ\text{C}$), and dried by pressing between filter papers. The salt is analytically pure.

At lower temperature (cooling of the salt solution in ice and filtering while cold), the decahydrate is obtained.

PROPERTIES:

White crystals, stable in air; isomorphous with $\text{Na}_2\text{SO}_4$. $d$ 3.21. Very readily soluble in water.

REFERENCE:

**Sodium Selenopentathionate**

\[ \text{Na}_2\text{SeS}_4\text{O}_6 \cdot 3\text{H}_2\text{O} \]

\[ \text{SeO}_2 + 4\text{Na}_2\text{S}_2\text{O}_3 + 4\text{CH}_3\text{COOH} \]

\[ 110.96 \quad 632.50 \quad 240.21 \]

\[ = \text{Na}_2\text{SeS}_4\text{O}_6 + \text{Na}_2\text{S}_4\text{O}_8 + 4\text{CH}_3\text{COONa} + 2\text{H}_2\text{O} \]

\[ 349.22 \quad 270.26 \quad 328.16 \quad 36.03 \]

A solution of 130 g. of Na\(_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}\) in 40 ml. of H\(_2\text{O}\) is prepared with heating; the solution is cooled to 25-30°C and is added dropwise over a period of 20 minutes with mechanical stirring to an ice-salt cooled solution of 17.2 g. of Fe\(_2\)O\(_3\) and 20 ml. of H\(_2\text{O}\) in 100 ml. of glacial acetic acid. The reaction temperature may not exceed 0°C. It is of utmost importance that the addition of Na\(_2\text{S}_2\text{O}_3\) be slow since thiosulfate catalyzes the decomposition of the selenopentathionate unless there is a constant excess of H\(_2\text{SeO}_3\). The clear, viscous, yellow-green solution is then mixed with 150 ml. of ethanol; after crystallization begins, 50 ml. of ether is added and the mixture is stirred and cooled for an additional 15 minutes. The crude product, containing about 40 g. of Na\(_2\text{SeS}_4\text{O}_6 \cdot 3\text{H}_2\text{O}\) and 4 mole percent of Na\(_2\text{S}_4\text{O}_8\), is filtered off, washed with ethanol and ether, and dried in vacuum over H\(_2\text{SO}_4\). To recrystallize the salt, it is dissolved in 50 ml. of 0.2N HCl at 30°C and suction-filtered; 100 ml. of methanol is added to the filtrate and the mixture is cooled in an ice-salt bath. Pure Na\(_2\text{SeS}_4\text{O}_6 \cdot 3\text{H}_2\text{O}\) crystallizes; it is filtered, washed with ethanol, and dried in vacuum over H\(_2\text{SO}_4\).

The yield is 25 g. (55%).

**PROPERTIES:**

Small, pale yellowish-green flakes. Very readily soluble in water, very soluble in methanol, insoluble in ethanol. Aqueous solutions are yellow-green and decompose gradually into selenium and tetrathionate; they can be stabilized by mineral acids; alkalis accelerate the decomposition. The pure salt can be stored over H\(_2\text{SO}_4\) for several months without decomposition (Se sometimes separates); readily loses its water of crystallization in vacuum over H\(_2\text{SO}_4\).

**REFERENCE:**

Selenium Sulfur Trioxide

\[ \text{Se} + \text{SO}_3 = \text{SeSO}_3 \]

78.96 80.07 159.03

Portions of liquid \( \text{SO}_3 \) are mixed with small quantities of selenium in a glass tube fused shut at one end and externally cooled with tap water. Between additions, the tube opening is closed with a one-hole stopper leading to a \( \text{P}_2\text{O}_5 \)-filled absorption flask. The reaction is exothermic; the temperature must be so adjusted that the \( \text{SO}_3 \) is just above its solidification point (about 15°C). The \( \text{SeSO}_3 \) product settles to the bottom and on the walls as a thick, dark-green oil which eventually solidifies. When all the Se has reacted, the supernatant clear \( \text{SO}_3 \) is decanted and any traces are removed by suction-filtration. The remaining scaly \( \text{SeSO}_3 \) is rapidly loosened from the walls with a sharp-edged glass rod and transferred to ampoules, which are sealed.

**PROPERTIES:**

Dark-green crystalline substance; stable for some time at room temperature without decomposition; sensitive to moisture. On heating, \( \text{SeSO}_3 \) decomposes, becoming first brown then yellow, then orange and finally red, and forming \( \text{SO}_2 \), \( \text{SeO}_2 \) and Se. Violent reaction with water, yielding \( \text{H}_2\text{SO}_4 \), \( \text{H}_2\text{SO}_3 \), \( \text{H}_2\text{SeO}_3 \) and Se. Soluble in oleum and concentrated sulfuric acid, giving a green solution.

**REFERENCES:**


Selenium Nitride

\( \text{Se}_4\text{N}_4 \)

**Caution!** \( \text{Se}_4\text{N}_4 \) is a very explosive substance. Even very small mechanical disturbances and mild action of chemicals cause extremely violent explosive decomposition. The strictest safety precautions must therefore be observed in handling this material.

**REACTION OF AMMONIA WITH DIETHYL SELENITE IN BENZENE SOLUTION**

The starting materials for preparing diethyl selenite are \( \text{C}_2\text{H}_5\text{ONa} \) and \( \text{SeOCl}_2 \). A solution of 20 g. of Na in 200 ml. of
absolute $C_2H_5OH$ is prepared in a reflux apparatus. When the reaction is complete, most of the $C_2H_5OH$ is distilled off and 70 g. of pure SeOCl$_2$ (p. 429) is allowed to drip onto the slurry; the latter is cooled with an ice bath and is frequently swirled around. The product, which has a strawberry color because of a slight Se precipitate, is extracted with ether and the ether solution dried with Na$_2$SO$_4$. Most of the ether is distilled off on a water bath, and the residue is fractionated twice in aspirator vacuum. The ester, a water-clear liquid, is collected between 83 and 85°C at 14 mm.

The conversion to Se$_4$N$_4$ is carried out in a 100-ml., round-bottom flask, closed with a three-hole rubber stopper. The stopper holds a separatory funnel, a gas inlet tube extending to the bottom, and a gas outlet tube leading to a drying tower filled with soda lime. Sodium-dried benzene (20 g.) is placed in the flask, and the apparatus is flushed with dry NH$_3$ until all air is displaced. The NH$_3$ stream is continued and 3.1 g. of diethyl selenite is slowly added drop-by-drop. An initially green suspension forms. The color soon turns to red-brown as N$_2$ is evolved. After 1.75 hours, the precipitate is suction-filtered and carefully dried at 105°C. To remove SeO$_2$ and Se, it is then successively washed with water, 10% KCN solution, and finally again with water to remove CN. Pure Se$_4$N$_4$ is best stored under benzene because of its explosive nature. The dry substance may not be placed in glass stoppered bottles since the contents generally explode when such bottles are opened. Cardboard boxes are the best containers.

Other preparative methods: Reaction of SeO$_2$, SeCl$_4$ or SeBr$_4$ with liquid ammonia in a steel autoclave at 70-80°C (Jander and Doetsch).

PROPERTIES:

Formula weight 371.87. Orange-red, amorphous powder; becomes crystalline after prolonged standing under benzene; under the influence of light pressure or strong heating, explodes with great brisance.

Insoluble in water; slowly decomposed by boiling water to yield $H_2SeO_3$, Se and NH$_3$. Slightly soluble in glacial acetic acid.

REFERENCES:


Tellurium

Te

Commercial tellurium must generally be further purified for most laboratory uses since it contains some TeO₂ as well as small amounts of Se, S and heavy metals (particularly Cu, Pb and Ag). It should be noted that Te is a strong respiratory poison. The metal is distilled in a hydrogen stream and converted to the readily crystallizable basic salt Te₂O₃(OH)NO₃; the latter is purified by repeated recrystallization, ignited to the oxide, and reduced in hydrochloric acid solution with hydrazine to form elemental Te. To achieve an ultrapure product, the metal is then distilled in high vacuum.

Prior to the prepurification by distillation in a hydrogen stream, the Te is pulverized in an agate mortar and placed in a large quartz boat inserted in the forward section of a quartz tube. The boat is gradually heated to red heat while a moderately fast stream of pure, dry hydrogen is passed over it. The Te melts and, with increasing temperature, gives off a greenish-yellow vapor which is carried along by the H₂ and condenses in small metallic balls in the colder section of the tube. The distillation is interrupted when about 90% of the Te has vaporized. All less volatile metals are found in the residue. After cooling in a stream of H₂, the distilled Te can be readily loosened from the tube wall and taken out with platinum forceps.

The prepurified product is dissolved in concentrated hydrochloric acid containing some nitric acid; excess nitric acid is decomposed by prolonged heating and the solution is diluted with water; taking care not to exceed the point at which hydrolysis (TeO₂ separation) would occur. The solution is filtered to remove any impurities which may be present, and is then reduced with freshly distilled hydrazinium hydroxide solution. The Te precipitate is washed with water and then alcohol and dried in a vacuum desiccator over concentrated H₂SO₄. The finely divided metal is then dissolved in nitric acid (d 1.25) at 70°C. Higher temperatures are to be avoided because of the precipitation of considerable quantities of rather insoluble TeO₂. As the solution is concentrated, the basic nitrate Te₂O₃(OH)NO₃ precipitates in large, well-formed crystals. The salt is again recrystallized from nitric acid of the same concentration. After drying, it is ignited to TeO₂ in a porcelain crucible in an electric furnace. The dioxide is dissolved in hydrochloric acid (d 1.12) and reduced to Te with hydrazinium hydroxide solution; the Te is washed and dried as above. Since the metal powder is always partially reoxidized...
to TeO₂ by atmospheric oxygen, the product powder is melted in a quartz boat while a pure hydrogen stream is passed over it. It is kept liquid until all the TeO₂ is reduced and the whole surface is shiny. To obtain an ultrapure product, the metal can then be distilled from a quartz boat placed in a quartz tube closed at one end; this is done in high vacuum and at as low a temperature as possible.

The purity of the product is determined most reliably by spectral analysis.

A process for preparing Te single crystals is given by Schmid and Wassermann; it involves melting the pure metal in narrow tubes, followed by very slow solidification.

REFERENCES:

Colloidal Tellurium Solution

Stable Te sols are obtained by the reduction of telluric acid with hydrazinium hydroxide.

A solution of 2-3 g. of very pure H₆TeO₆ (p. 451) in one liter of very pure water (see section on Hydrogen, Deuterium, Water, p. 117) is prepared and heated on a water bath to 40-50°C. Higher temperatures may cause a yellow color in the subsequent reduction. A very dilute aqueous N₂H₄ solution (1 : 2000) is added dropwise to the warm H₆TeO₆ solution until the color of the hydrosol no longer changes. An excess of reducing agent should be avoided since it renders the sol very unstable and causes coagulation. The liquid is transferred into a dialyzer or parchment paper bag and is dialyzed until completely pure; the exterior water is frequently renewed.

REFERENCES:

Hydrogen Telluride

\[ \text{H}_2\text{Te} \]

Since H₂Te is a poisonous gas with an unpleasant odor and, when inhaled in large quantities, greatly irritates the bronchial
tubes and damages the nervous system, its preparation must be carried out in a good hood and in carefully sealed apparatus.

I. CATHODIC REDUCTION OF Te

Electrolytic preparation of H₂Te is generally preferred to the method of acid decomposition of tellurides (see II) because the yield is higher.

The apparatus of Fig. 169 is used. The electrolysis flask proper, which is made of glass, stands in a zinc tub surrounded by thermal insulation and an external wooden box. The cathode is introduced from below through adapter tube C. The cathode is made from a thin-wall glass tube which is fused and closed at one end. A few grams of pure Te are melted in the tube and a copper wire is inserted before the melt solidifies. After cooling, the space above the Te is filled with plaster of Paris. The tube tip at the tellurium end is then cracked by scratching, warming it slightly, and immersing it in water. The tellurium is thus exposed. The anode is of platinum foil. The electrolysis vessel is filled to the upper edge of the anode with 50% sulfuric acid and is cooled from the outside by a Dry Ice bath. The run is conducted in a darkened room since, according to Hempel and Weber, H₂Te decomposes more rapidly in light. The electrolysis proceeds at 4.5 amp. and 75-110 v., and the pressure is so adjusted that only a thin layer of acid is found above the Te at the cathode. The electrolyte temperature is maintained at 0°C by balancing the exterior cooling and the heat produced by the current. The evolving gas mixture, which contains up to 45% H₂Te (besides the H₂), is dried by passage through two U tubes containing CaCl₂ and P₂O₅-glass wool (no rubber connections may be used), and is then condensed in a trap cooled with liquid nitrogen. As usual, the trap is protected against atmospheric moisture by a drying tube. The gas obtained after reevaporation is sufficiently pure for most purposes.
If a very pure product is required, the traces of inert gas are removed by repeated melting and solidification in vacuum by fractionation or sublimation in high vacuum; a considerable amount of the first and last cuts is rejected.

Hydrogen telluride is stored in the dark either as a solid at low temperature or in the vapor state in torch-sealed glass flasks. Mercury may not be used as a sealing liquid since it is attacked even by carefully dried $H_2Te$.

The $Al_2Te_3$ used as starting material is prepared from the elements according to the method of Moser and Ertl (see section on Aluminum).

The acid decomposition is carried out in the apparatus shown in Fig. 170, which permits the introduction of the telluride into the acid in an inert gas stream. All parts of the apparatus must be carefully dried before assembly since $H_2Te$ is decomposed by moisture, with Te precipitation. Hydrochloric acid (4N) is boiled and then cooled in a $N_2$ stream. The reaction flask $E$ (100 ml.) is filled with this acid. The entire experiment is done in an atmosphere of pure $N_2$, which is introduced through the side arm $U$ and the hollow piston rod $S$ whose conical end fits into the ground glass joint $H$ of adapter $A$. When the air has been displaced from the apparatus, coarsely powdered $Al_2Te_3$ is rapidly introduced at $T$. By tilting or slight tapping of the apparatus, the powder is gradually transferred into adapter $A$; by slight downward motion of the piston rod, small portions are introduced into the acid. At the end, flask $E$ is heated to a moderate temperature for a short time in order to complete the gas evolution. The $H_2Te$ passes through a small water-cooled condenser which forms a side
arm of $E$ and through two drying tubes filled with CaCl$_2$ and P$_2$O$_5$-glass wool, and is frozen in a trap cooled with liquid nitrogen and protected against moisture by a drying tube. When pure starting materials are used, the product is generally sufficiently pure; it can be further fractionated via the procedure given in method I.

**PROPERTIES:**

Formula weight 129.63. Colorless gas, unpleasant odor reminiscent of AsH$_3$; poisonous. Decomposes with Te separation with even traces of air or moisture, also with cork and rubber. Whenever possible, ground glass joints should therefore be used. The liquid is instantaneously decomposed by light, which produces discoloration; whether or not light accelerates the decomposition of the gas as well is not certain as the data existing in the literature are contradictory. According to Moser, pure dry H$_2$Te is stable even in ultraviolet light.

M.p. $-49^\circ$C, b.p. $-2^\circ$C. Begins to decompose into the elements slightly above room temperature. d (liq.) ($-12^\circ$C) 2.68; weight per liter 6.234 g.

Soluble in water with rapid decomposition; the saturated solution is about 0.1N.

**REFERENCES:**


**Sodium Telluride, Potassium Telluride**

Na$_2$Te, K$_2$Te

\[
2 \text{Na} + \text{Te} = \text{Na}_2\text{Te} \\
45.99 + 127.61 = 173.60
\]

\[
2 \text{K} + \text{Te} = \text{K}_2\text{Te} \\
78.10 + 127.61 = 205.80
\]

The synthesis is carried out in liquid NH$_3$ with exclusion of air and moisture. For the apparatus and procedure, see K$_2$S (p. 360). The directions may be followed in all details; the compounds Na$_2$Te and K$_2$Te prepared accordingly are analytically pure.

**PROPERTIES:**

Na$_2$Te: White crystalline powder; very hygroscopic; decomposes immediately in air, becoming dark; crystallizes in the C1
structure type. M.p. 953°C; d 2.90. Soluble in water; on contact with air, the solution rapidly precipitates black Te powder.

K₂Te: Faintly yellow, crystalline substance; hygroscopic; decomposes instantaneously on contact with air with Te precipitation. Crystallizes in C₁ structure type. d 2.52. Soluble in water; the solution precipitates Te in air.

REFERENCE:

**Sodium Ditelluride**

\[
\text{Na}_2\text{Te}_2
\]

\[
\text{Na}_2\text{Te} + \text{Te} = \text{Na}_2\text{Te}_2
\]

173.60 127.61 301.21

The stoichiometric quantity of Te and 2.5 g. of Na₂Te are introduced in a rapid stream of pure N₂ into a Pyrex tube, closed at one end. The tube is evacuated with a high-vacuum pump, the open end is melted shut under vacuum, and the tube is heated in an electric furnace to 500°C until a homogeneous melt is formed (about 45 min.). After cooling, a gray-black, very hard mass of Na₂Te₂ is obtained.

**PROPERTIES:**

Gray-black, metallic, shiny microcrystalline substance; decomposes in the presence of air and moisture.

**REFERENCES:**

**Tellurium Tetrachloride**

\[
\text{TeCl}_4
\]

\[
\text{Te} + 2\text{Cl}_2 = \text{TeCl}_4
\]

127.61 141.83 269.44

The synthesis is carried out in the glass apparatus shown in Fig. 171; because of the extreme hygroscopicity of TeCl₄, all
connections are glass fused to glass. The number of sealable ampoules \( A_1, A_2, \) etc., can be varied depending on the number of individual samples desired. The apparatus is dried in a drying oven for 12 hours prior to the run. Then 50 g. of pure Te (powder or coarse fragments of Te sticks) is placed in the still warm flask \( K \) through \( H \). Opening \( H \) is then closed, \( c \) is clamped shut, and the whole apparatus is heated by fanning with a flame to remove the last traces of water film; at the same time, the apparatus is evacuated through \( d \). When the apparatus is cooled down, the connection to the vacuum line is broken and the apparatus is rinsed with dry, \( O_2 \)-free \( N_2 \) introduced at \( c \). When all air is displaced, a slow stream of dry, \( O_2 \)-free \( Cl_2 \) (p. 272) is introduced and \( K \) is carefully heated at the same time with a Bunsen burner to initiate the reaction. The flame can be removed as soon as the reaction starts. The contents of the flask liquefy after some time. They turn black at first, then transparent and dark red, and finally amber yellow. Toward the end of the reaction, \( K \) is again slightly heated. When the product has become pure yellow, dry \( Cl_2-HCl \) mixture is passed through for some time with slight heating, in order to decompose any oxychloride that might have formed. At the end, the product is distilled into the ampoules in a slow \( Cl_2 \) stream, the heat being supplied by fanning with a flame. The ampoules are then sealed. The yield is 95 g. of pure \( TeCl_4 \).

**PROPERTIES:**

Fine, white crystals; very hygroscopic; deliquesces in moist air with partial hydrolysis. M.p. 224°C, b.p. 390°C; d 3.01. The melt is yellow, the vapor orange-red.

Hydrolyzes with water to form \( HCl \) and \( TeO_2 \). Soluble in absolute alcohol and toluene.
REFERENCES:


Hexachlorotellurium Salts

The required stock solution of TeCl$_4$ in hydrochloric acid is best prepared by treating Te powder with aqua regia, evaporating this solution to dryness, and taking up residue in as little concentrated hydrochloric acid as possible.

$$(\text{NH}_4)_2\text{TeCl}_6$$

$$\text{TeCl}_4 + 2\text{NH}_4\text{O} = (\text{NH}_4)_2\text{TeCl}_6.$$  
269.43 106.99 376.42

Concentrated aqueous NH$_4$Cl solution is added to the TeCl$_4$ solution in hydrochloric in such a quantity that the mixture is just at the point of NH$_4$Cl precipitation. On prolonged standing in air, the yellow complex salt precipitates in beautiful, relatively large octahedra. The precipitation can be accelerated and completed by passage of HCl and cooling. The salt is considerably less moisture-sensitive than the analogous selenium compound. After suction-filtration and pressing between filter papers, it can therefore be dried in air and stored in a desiccator.

$$_3\text{K}_2\text{TeCl}_6$$

$$\text{TeCl}_4 + 2\text{KCl} = _3\text{K}_2\text{TeCl}_6.$$  
269.43 149.10 418.53

The TeCl$_4$ solution is mixed with aqueous KCl solution in a ratio not exceeding one mole of KCl per mole of TeCl$_4$; precipitation should not be allowed to occur. The precipitation procedure corresponds to that for (NH$_4$)$_2$TeCl$_6$. Since the K salt is considerably more sensitive to atmospheric moisture than the NH$_4$ salt, it is best to dry it in the apparatus described for the preparation of hexachlorotitanium salts (see section on Titanium).

The Rb and Cs chloro complex salts are prepared analogously. For the preparation of Tl$_2$TeCl$_6$, see G. Engel.
PROPERTIES:

\[
[(\text{NH}_4)_2\text{TeCl}_6 \text{ and K}_2\text{TeCl}_6]:\text{ yellow, octahedral crystals, about 0.1 mm \ in \ diameter; decompose gradually in air, particularly when moistened with hydrochloric acid, with color loss and HCl evolution. The NH}_4\text{ salt is considerably more stable than the K salt. Both are very readily soluble in water, hydrolyzing to tellurous and hydrochloric acids. Dissolve without decomposition in not too dilute hydrochloric acid, the K salt more readily than the NH}_4\text{ salt. The latter can be recrystallized from hydrochloric acid.}
\]

CRYSTAL STRUCTURE:

\[
[(\text{NH}_4)_2\text{TeCl}_6 : \text{ K}_2\text{PtCl}_6]:\text{ structure type; K}_2\text{TeCl}_6;\text{ optically uniaxially negative crystal; monoclinic, pseudocubic lattice; deviation from the K}_2\text{PtCl}_6\text{ structure type is only slight.}
\]

REFERENCES:


Tellurium Tetrabromide

\[
\text{TeBr}_4
\]

\[
\text{Te} + 2\text{Br}_2 = \text{TeBr}_4
\]

127.61 319.66 447.27

Pure Te (5 g.) is introduced through adapter \(a\) into the elongated reaction flask \(A\) of the apparatus shown in Fig. 172. Adapter \(a\) is connected to a \(N_2\) purification train which furnishes either pure dry \(N_2\) or \(N_2\) containing bromine vapor. For the latter, the gas stream may be passed through a wash bottle containing dry \(\text{Br}_2\), followed by a U tube containing \(\text{P}_2\text{O}_5\)-glass wool. First, the apparatus is purged with pure \(N_2\). Then \(A\) is cooled with ice water and the \(N_2\)-\(\text{Br}_2\) mixture is introduced. A portion of the \(\text{Br}_2\) condenses on the Te and reacts quietly with it, while the remainder is retained in the empty U tube \(D\), cooled with an ice-salt mixture. The difference between the weight loss of the \(\text{Br}_2\) wash bottle and the weight of the condensate in \(D\) indicates the amount of bromine remaining in \(A\). When this becomes about twice the amount needed for quantitative conversion to \(\text{TeBr}_4\), the gas stream is interrupted, stopcock \(C\) is closed, and the product slurry is allowed to stand at room temperature for several hours (better overnight) in order to complete the reaction. Then \(C\) is reopened and the excess
bromine is purged by a stream of N\textsubscript{2} while \( A \) is simultaneously heated to 50\textdegree C. To purify the product, it is sublimed in vacuum. Gas inlet tube \( a \) is sealed off at \( d \), the whole apparatus is tilted to a horizontal position, and ground glass joint \( E \) is connected to an aspirator through a P\textsubscript{2}O\textsubscript{5} drying tube. During evacuation, \( A \) is heated to sublimation temperature (about 350\textdegree C) with an electric furnace. Any black condensate which may separate in \( B \) at 200\textdegree C is vaporized by heating with a burner. The subsequently deposited yellow to orange-red powder is quite pure TeBr\textsubscript{4}; if necessary, this can be further purified by an analogous sublimation in high vacuum. Because of its hygroscopicity, the product is either immediately sealed in the condensation receiver or is rapidly transferred to a well-sealed vessel.

**Properties:**

Yellow to orange, hygroscopic crystals. On heating, partially decomposes with Br\textsubscript{2} evolution; for this reason, TeBr\textsubscript{4} cannot be melted or distilled at atmospheric pressure without decomposition. \( d \) (15\textdegree C) 4.31.

Hydrolyzes in water; soluble in hydrobromic acid, ether and glacial acetic acid.

**References:**

B. Brauner, Mh. Chem. 10, 411 (1889).
Tellurium Tetraiodide

TeI₄

\[
\text{Te(OH)}_6 + 6 \text{HI} = \text{TeI}_4 + \text{I}_2 + 6 \text{H}_2\text{O}
\]

A very concentrated H₃TeO₅ solution (p. 451) is mixed at room temperature with slightly more than the stoichiometric quantity of fuming hydriodic acid (d 2.00). A heavy, gray precipitate of TeI₄ immediately separates. It is suction-filtered on a fritted glass filter and freed of traces of hydriodic acid by pressing on clay. Concentration of the mother liquor at room temperature yields a considerable additional amount of the compound. When dry, the crystals are washed several times with pure CCl₄ to remove iodine and are finally pulverized under CCl₄ until the continuously renewed wash fluid no longer is colored. The product is then analytically pure.

PROPERTIES:

Iron-gray crystalline substance; stable even in moist air. Decomposes on heating, giving off I₂. M.p. (closed tube) 280°C; d (15°C) 5.05. Hydrolyzed slowly in cold water, rapidly in warm water, forming TeO₂ and HI. Soluble in hydriodic acid, forming H(TeI₅); slightly soluble in acetone.

REFERENCES:


Tellurium Dioxide

TeO₂

\[
2 \text{Te} + 9 \text{HNO}_3 = \text{Te}_2\text{O}_3(\text{OH})\text{NO}_3 + 8 \text{NO}_2 + 4 \text{H}_2\text{O}
\]

Concentrated nitric acid (95 ml.; d 1.42) is slowly added to a suspension of 20 g. of Te powder (commercial grade) in 200 ml. of distilled water in a one-liter beaker. The mixture is allowed to
stand for about 10 minutes with occasional shaking. Any impurities which have not dissolved after this time (selenides, tellurides, etc.) are rapidly suction-filtered, and the filtrate is mixed with another 65 ml. of concentrated nitric acid. The solution is boiled until all oxides of nitrogen are removed. If the Te contained any Sb or Bi, the basic nitrates of these elements separate and, if necessary, are filtered through a fritted glass suction filter. The clear solution is concentrated to 100 ml. on a water bath, using a 600-ml. beaker; it is then allowed to cool and is suction-filtered to remove the crystallized \( \text{Te}_2\text{O}_3(\text{OH})\text{NO}_3 \). The salt is washed with water and dried on clay in air. In order to convert it to \( \text{TeO}_2 \), it is heated for two hours at 400-430°C (sand bath or hotplate) in a porcelain dish protected from dust by an inverted beaker (to avoid reduction to Te). The \( \text{TeO}_2 \) product is pure white and is analytically pure. If the starting material is very impure, the \( \text{Te}_2\text{O}_3(\text{OH})\text{NO}_3 \) may again be recrystallized from nitric acid (d 1.25) before the ignition. Immediately after cooling, the pure product is transferred into a tightly sealed clean vessel to prevent any discoloration by the reducing action of organic substances in the atmosphere. Assuming that good quality commercial Te is used, the yield is about 21 g. or 84%.

II. \( \text{H}_6\text{TeO}_8 = \text{TeO}_2 + \frac{1}{2} \text{O}_2 + 3 \text{H}_2\text{O} \)

\[
\begin{array}{cccc}
229.66 & 159.61 & 16.00 & 54.05 \\
\end{array}
\]

Pure \( \text{H}_6\text{TeO}_8 \) (p. 451) is heated in a porcelain crucible. The heating is done in two stages: first the material is heated slowly to 150-200°C until most of the water is driven off; then it is ignited for some time at about 600°C. If the conversion to \( \text{TeO}_2 \) is quantitative, the crucible contents are pure white after cooling. If the material is yellowish, the product still contains \( \text{TeO}_3 \) and must be heated further. The purity of the \( \text{TeO}_2 \) product is determined by that of the \( \text{H}_6\text{TeO}_8 \) used.

PROPERTIES:

White crystals; not hygroscopic; discolors in the presence of organic materials because of partial reduction. M.p. 733°C; the melt is dark yellow. d 6.02.

Very slightly soluble in water (about 1 : 150,000); soluble in concentrated mineral acids and alkalis, with salt formation.

Crystallizes in C 4 structure type.

REFERENCES:


**Tellurous Acid**

\[ \text{H}_2\text{TeO}_3 \]

The \( \text{K}_2\text{TeO}_3 \) stock solution is made by dissolving pure Te (p. 437) in dilute HNO\(_3\), evaporating to dryness, and dissolving the residue in 10% KOH. The solution is colored with one drop of phenolphthalein and mixed at 0°C with dilute HNO\(_3\), added dropwise from a burette, until it is colorless. A white — first flaky, then finely powdered — precipitate of \( \text{H}_2\text{TeO}_3 \) separates. It is filtered and thoroughly washed with ice water until the wash water is free of NO\(_3^-\) and K\(^+\) ions. The product is stored under distilled water since, in the dry state, it readily loses H\(_2\)O, forming TeO\(_2\) hydrates of lower water contents.

**PROPERTIES:**

White, amorphous substance of varying composition; H\(_2\)O content is frequently less than that corresponding to the formula H\(_2\)TeO\(_3\); loses water when dry but can be stored under H\(_2\)O for several days without change.

On heating above room temperature, extensively loses water with conversion to TeO\(_2\). Very slightly soluble in water (at 18°C about 3.0 \( \times \) 10\(^{-3}\) moles/liter).

**REFERENCES:**


**Sodium Tellurite**

\[ \text{Na}_2\text{TeO}_3 \]

Stoichiometric quantities of pure TeO\(_2\) (p. 447) and C. P. Na\(_2\)CO\(_3\) are melted together in a Pt crucible. In order to prevent
oxidation to tellurate, the heating must be carried out in a CO$_2$ atmosphere. As soon as gas evolution stops and a clear melt is obtained, the latter is allowed to cool under CO$_2$. The white crystalline mass is Na$_2$TeO$_3$.

**PROPERTIES:**

White crystalline substance; converts to Na$_2$TeO$_4$ when heated in air.

Very readily soluble in water; the solution is decomposed by atmospheric CO$_2$, yielding TeO$_2$.

**REFERENCE:**


**Tellurium Trioxide**

TeO$_3$

$$H_6TeO_8 = TeO_3 + 3 H_2O$$

229.66 175.61 54.05

I. $\alpha$-TeO$_3$

Pure $H_6TeO_8$ (p. 451) is slowly heated to 300-320°C in a porcelain crucible with occasional stirring. When all the H$_2$O has been driven off, the material is cooled and mixed several times with concentrated hydrochloric acid to remove any TeO$_2$ which might have formed. The washing flask should be cooled. The pure TeO$_3$ is then thoroughly washed with water and dried at 100°C. The yield is about 30%.

**PROPERTIES:**

Bright yellow powder which, in contrast to $\beta$-TeO$_3$, gives no powder pattern.

On heating, $\alpha$-TeO$_3$ becomes brown at about 200°C, and above 400°C decomposes to TeO$_2$ and O$_2$. $d$ (15°C) 5.075.

Nearly insoluble in cold water, but noticeably soluble on long standing in hot water, forming $H_6TeO_8$. Soluble in strong alkali, forming tellurates.

II. $\beta$-TeO$_3$

Pure $H_6TeO_8$ is mixed with a few drops of concentrated $H_2SO_4$ and heated for 12-15 hours at about 320°C in a torch-sealed tube.
In order to remove $\alpha$-TeO$_3$, the product is then boiled with concentrated KOH solution and the resulting solution is filtered with suction through a fritted glass filter. The $\beta$-TeO$_3$ product is washed thoroughly with water and dried at 100°C. The yield is about 40%.

**PROPERTIES:**

Gray, microcrystalline substance which, in general, is considerably less reactive than $\alpha$-TeO$_3$. On heating above 400°C, decomposes into TeO$_2$ and O$_2$. $d$ 6.21.

Insoluble in water; even hot acids and concentrated alkali do not attack it and do not form salts.

**REFERENCES:**


**Telluric Acid**

$$H_6TeO_6$$

The starting materials are very fine Te powder and aqueous HClO$_3$ solution. The acid required for the oxidation of 0.1 mole (that is, 12.75 g.) of Te is prepared by adding a lukewarm mixture of 40 ml. of H$_2$O and 7.2 ml. of concentrated H$_2$SO$_4$ to a solution of 24 g. of Ba(ClO$_3$)$_2$·H$_2$O in 100 ml. of H$_2$O. After about five hours, the solution is decanted from the precipitated BaSO$_4$ through a filter, and if desired the residue is extracted once with H$_2$O. To oxidize the Te, it is added to a 500-ml., round-bottom flask placed under the hood. It is then moistened with 5 ml. of 50% HNO$_3$ and about one fourth of the HCIO$_3$ solution. With thorough agitation (by swirling) the flask contents soon boil and the reaction proceeds at boiling with strong Cl$_2$ evolution to form H$_6$TeO$_6$. The reaction should definitely not be slowed by intermittent cooling. If white flakes (H$_2$TeO$_3$ or TeO$_2$) should form in the liquid, the contents of the flask must be continuously boiled. As soon as the evolution of Cl$_2$ subsides, the rest of the HCIO$_3$ solution is added in several large portions while the solution is again kept boiling and is constantly agitated. After 30 minutes, the reaction is complete and all the Te should be dissolved. The clear liquid is now concentrated in a porcelain dish, first over a free flame and
finally on a water bath, until crystals begin to separate (the solution volume is about 1/3 of the original at this point). The dish is then set on ice; the acid separates with stirring as a fine, pure-white crystalline powder. The precipitate is suction-filtered through fritted glass and dissolved once more in hot distilled H₂O in order to remove traces of HCl. The solution is mixed with a few drops of dilute AgNO₃. After filtering off the AgCl, the solution is evaporated until crystallization begins. When the liquid is cooled slowly, the acid separates in beautiful, water-clear crystals up to 2 cm. long. It is suction-filtered through fritted glass, washed with water at 0°C, then with alcohol and ether, and dried in a vacuum desiccator over P₂O₅. By mixing the mother liquor with an equal volume of alcohol, a further finely crystalline fraction, somewhat more soluble in cold H₂O, may be obtained. The total yield is 90-95%.

Other preparative methods:

II. OXIDATION OF TeO₂ WITH KMnO₄ IN NITRIC ACID SOLUTION:

\[ 5 \text{TeO}_2 + 2 \text{KMnO}_4 + 6 \text{HNO}_3 + 12 \text{H}_2\text{O} \]
\[ = 5 \text{H}_6\text{TeO}_6 + 2 \text{KNO}_3 + 2 \text{Mn(NO}_3)_2. \]

The process is somewhat more cumbersome than method I since it requires, among other things, separate preparation of TeO₂ as well as repeated recrystallization of the acid to quantitatively remove the simultaneously formed salts. The yield is 75-85%. For detailed description of the procedure, see the literature below.

III. Reaction of Te or TeO₂ with 30% H₂O₂ in sulfuric acid or alkaline solution and subsequent precipitation of H₆TeO₆ with concentrated nitric acid.

IV. Oxidation of Te with HNO₃ and CrO₃. The product must be recrystallized several times in order to remove the Cr(NO₃)₃ by-product.

PROPERTIES:

Formula weight 229.66. Colorless crystals, stable in air. May occur in a monoclinic modification (space group C₂h) and a cubic modification (space group O₅); the large crystals are generally monoclinic while the microcrystalline powder frequently consists of a mixture of both forms.

Heating H₆TeO₆ between 100 and 220°C converts it to solid, water-insoluble polymetalluric acid; the latter decomposes above 220°C into TeO₃, and at 400°C or higher into TeO₂ and O₂. Melts in a sealed tube at about 136°C, forming a concentrated aqueous solution of polymetalluric acid and some polyorthometalluric acid, d (monoclinic) 3.071; d (cubic) 3.17.
Readily soluble in water; very slightly soluble in concentrated nitric acid.

REFERENCES:


**Sodium Tetrahydrogentellurate (VI)**

\[
Na_2H_4TeO_6 + 2NaOH = Na_2H_4TeO_6 + 2H_2O
\]

A moderately concentrated \( H_6TeO_6 \) solution (p. 451) is mixed at the boiling point with the stoichiometric quantity of concentrated NaOH solution and is kept boiling for a short time. A microcrystalline, granular precipitate of \( Na_2H_4TeO_6 \) separates. When the solution has cooled, it is filtered by suction, washed with water at 0°C, and dried in a desiccator over \( CaCl_2 \). The salt thus obtained is analytically pure.

**PROPERTIES:**

White crystals, stable in air. Decomposes into \( Na_2TeO_3 \) when vigorously heated. Very slightly soluble in water.

REFERENCES:

A. Rosenheim and G. Jander, Kolloid-Z. 22, 23 (1918).

**Sodium Orthotellurate**

\[
Na_4TeO_6
\]

\[
H_6TeO_6 + 6NaOH = Na_4TeO_6 + 6H_2O
\]

Solid NaOH is melted in a porcelain crucible and the stoichiometric quantity of \( H_6TeO_6 \) is added to the melt at 290-300°C.
When the reaction is complete, the crucible is slowly cooled, then broken; alcohol is poured over it and allowed to stand for 4-5 hours. The solution thus formed is filtered hot and slowly concentrated at room temperature until crystallization occurs. After 2-3 days, crystals (1-1.5 cm. long) of Na₅TeO₆·2H₂O separate. The product is filtered off, washed with alcohol, and dried in a vacuum desiccator over P₂O₅. The water of crystallization is given off quantitatively, and the product converts to white, powdery Na₅TeO₆. The salt thus obtained is analytically pure.

II. Other Preparative Methods: Fusing Na₂O and Na₂TeO₄ at 700°
The process requires a large amount of equipment. Detailed descriptions of the apparatus and procedure are given in the literature below.

PROPERTIES:

White, microcrystalline powder; gradually forms Na₂H₄TeO₆·3H₂O in air. Readily soluble in water.

REFERENCES:


Sodium Telluropentathionate
Na₂TeS₄O₆·2H₂O

TeO₃ + 4 Na₂S₂O₃ + 4 CH₃COOH
159.61 632.50 240.21

= Na₂TeS₄O₆ + Na₅S₄O₆ + 4 CH₃COONa + 2 H₂O
397.87 270.26 328.16 36.03

Under the same conditions as those described for the preparation of Na₂SeS₄O₆·3H₂O (p. 434), 110 g. of Na₂S₂O₃·5H₂O is dissolved in 60 ml. of H₂O and then added over a period of 15 minutes to a solution of 18.8 g. of TeO₂ in 75 ml. of concentrated HCl and 75 ml. of glacial acetic acid. Then 150 ml. of ethanol is added and the mixture is stirred and cooled for 15 additional minutes. Rubbing the walls with a glass rod accelerates the crystallization.
The crude product, which contains approximately 25 g. of Na₂TeS₄O₆·2H₂O and 2-4 mole percent of Na₂S₄O₆, is filtered, washed with ethanol and ether, and dried in vacuum over H₂SO₄.

To recrystallize the salt, it is dissolved in 60 ml. of 0.2N HCl held below 45°C; further procedure is as in the preparation of Na₂SeS₄O₆·3H₂O. The yield is 20 g. (45%).

**PROPERTIES:**

Small flakes or flat needles. In large quantities, the crystals appear yellow with an orange cast; individual crystals seem yellow with a greenish cast. Dilute aqueous solutions seem yellow, concentrated ones orange-red. Completely soluble in water but less soluble than the corresponding selenium salt. Aqueous solutions gradually decompose into Te and tetrathionate but the rate of decomposition is smaller than that of the corresponding selenium salt. The solutions can be stabilized by mineral acids, whereas alkalis accelerate the decomposition. Insoluble in ethanol, very slightly soluble in methanol. Readily gives off its water of crystallization over H₂SO₄ in vacuum. The pure material can be stored over H₂SO₄ for several months without decomposition (Te eventually separates).

**REFERENCE:**


**Tellurium Sulfur Trioxide**

\[
\text{Te} + \text{SO}_3 = \text{TeSO}_3
\]

An excess of molten SO₃ is allowed to react with pure, finely powdered Te at room temperature. The reaction must be protected from moisture. The apparatus and the procedure are the same as for the analogous synthesis of S₂O₃ (p. 380). The product is dark-red α-TeSO₃; in order to obtain the light brown β-modification, this product is heated for a short time to about 80°C.

Stored in ampoules sealed in an oxygen-free atmosphere at pressures below 1 mm. When so stored, it is stable for some time at room temperature.
7. SULFUR, SELENIUM, TELLURIUM

PROPERTIES:

The α-modification is dark, and the β-form is light brown; very hygroscopic; decomposes on heating above 90°C into SO₂, TeO₂ and Te.

Reacts violently with water, resulting in the precipitation of Te and formation of H₂SO₄, H₂SO₃ and H₂TeO₃. Soluble in oleum with a blood-red color; insoluble in pure SO₃.

REFERENCES: