SECTION 11

Carbon

a) Elemental Carbon

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Only processes of special importance to the laboratory will be discussed below. The corresponding industrial processes are not described.


Pure Carbon

The carbon available for industrial or laboratory purposes is not pure. It contains carbon compounds (with H, O, N, S), ash-forming constituents and adsorbed gases or vapors. Preparation of highest-purity carbon, as well as its use in the pure state, may be achieved only in a high-vacuum apparatus [A. Stock et al. Z. anorg. allg. Chem. 195, 158 (1931)]. Purity in excess of 99% is usually sufficient. This may be achieved by the following processes, which apply equally to coke-type carbon, carbon black, activated charcoal or graphite.

Removal of ash-forming mineral matter. Exhaustive boiling with dilute HNO₃ or dilute HCl; ignition to red heat at 900 to 1000°C in a stream of Cl₂; treatment with hydrofluoric acid to remove silicates; calcining for several hours at 2000 to 3000°C in vacuum, in CO or in inert gas (this treatment results in structural changes, i.e., graphitization).

Removal of carbon compounds (coking). Solvents are incapable of removing all of these constituents. Complete removal is achieved by calcining for many hours in vacuum or in H₂, N₂ or inert gas at 900 to 1000°C. If more than a few percent of carbon compounds are present before calcination, the additional formation of C from these carbon impurities will result in structural changes. These structural changes tend chiefly to reduce adsorptive power. This difficulty can be overcome by activation (q.v.) without affecting the purity of the carbon.
Surface oxides (q.v.) can be completely removed as CO and CO$_2$ at 1000°C.

Removal of adsorbed gases and vapors. It must be borne in mind that adsorptive carbon can take up a few percent by weight of CO$_2$, H$_2$O, etc., at room temperature. Purification is achieved by heating for many hours at 300°C in high vacuum.

REFERENCES:


Special Carbon Preparations

I. CARBON MONOXIDE BLACK

This carbon black deserves more attention because medium-sized graphite crystals of it undergo little aggregation. It is prepared by passing CO over finely divided, pure Fe (e.g., pure iron prepared by reduction of iron carbonyl) at 400-700°C. Depending on the temperature of preparation, the following average crystal sizes are obtained: 50 Å at 400°C, 100 Å at 500°C, 200 Å at 700°C. It should be remembered that any occluded Fe compounds can be removed only by a long purification process (see Pure Carbon).

II. GRAPHITIZED CARBON BLACK

Calcination in vacuum or protective gas for many hours at 2000-3000°C causes the crystallites of the individual carbon black particles to grow into slightly larger crystals, without significantly affecting the size of the particles themselves (channel black about 200 Å, lamp black 500-2000 Å, Thermatomic black about 3000 Å). The product of the calcination is a polyhedron consisting of slightly pyramidal graphite crystals with their vertices directed inward, with its surface composed of the basal planes (001) of graphite.

III. GRAPHITE OXIDE BLACK

This black consists of very thin graphite foils (about 20 to 50 Å thick) the diameter of which, however, may range up to some hundreds of a millimeter, depending on the starting graphite. It is prepared by making graphite oxide from graphite (see Graphite Oxide). The graphite oxide is decomposed by rapid heating to
300-400°C, where it deflagrates. Since the oxygen bound in the graphite oxide evolves as CO and CO$_2$ in the deflagration, it is possible that the hexagonal network of the carbon black foils contains holes of atomic dimensions.

A better product of otherwise identical properties can be prepared as follows: An alkaline suspension of graphite oxide is reduced with hydroxylamine at 80°C. The agglutination of the foils upon filtering and desiccation can be substantially inhibited by freeze-drying of the salt-free, dialyzed suspension.

In both cases the carbon black contains only about 80% carbon. It also contains O, H, etc., and must be carefully purified by coking and, if necessary, also freed of mineral matter.

IV. LUSTROUS CARBON

Brittle foils with perfectly reflecting surfaces because the basal planes of the graphite crystals are parallel to the foil planes. Surfaces up to several centimeters. Thicknesses up to some tenths of a millimeter. Coatings of lustrous carbon on ceramic materials serve as high electrical resistances. The crystal size is about 25 Å.

The material is prepared by cracking dilute hydrocarbons (e.g., propane vapor at about 10 mm. or N$_2$ saturated with gasoline vapor at room temperature) at 800 to 1000°C. The material is deposited on a smooth surface such as porcelain or quartz. It is desirable to add some O$_2$ or water vapor to the hydrocarbon, so as to avoid simultaneous precipitation of reactive, rough-surface carbon. After a thickness of some hundredths of a millimeter has been achieved, the carbon foils either flake off by themselves or may be readily detached after cooling. The best tightly adhering coatings are produced on surfaces that are not completely smooth.

V. GRAPHITE FOILS AND FILMS

a) A sol prepared from 1-2 g. of graphite oxide (q.v.) in 100 ml. of water (well shaken or stirred) is allowed to evaporate. The graphite oxide separates as a foil on the bottom of the vessel. Very careful, slow heating with gradually rising temperature causes the sheet to give off CO, CO$_2$ and H$_2$O without deflagration until, at 1000°C, a graphitelike film is obtained. This still contains a few percent of O and H. The size and thickness of the foil is the same as that of the graphite oxide and can therefore be controlled by the amount and concentration of the graphite oxide sol and the size of the vaporization vessel. Films with surfaces as large as 50 cm$^2$ can be obtained in this manner.

b) Very pure graphite foils can be produced by igniting foils of lustrous carbon for many hours in vacuum or in CO. The
temperature is 2000-3000°C. The foils are of the same size as those of lustrous carbon, i.e., about 1 cm. in surface diameter.

VI. ADSORPTIVE CARBON (ACTIVATION)

To achieve the best adsorptive power, it is helpful to break down the crystalline aggregations of carbon by careful oxidation. A carbon is considered highly adsorptive if, for example, it adsorbs its own weight of CC\textsubscript{4} at room temperature from half-saturated CC\textsubscript{4} vapor.

This breaking down of structure is effected most simply by calcining at 950°C in a stream of CO\textsubscript{2} or H\textsubscript{2}O vapor and is continued until half the carbon has burned off. It suffices to pass the CO\textsubscript{2} slowly over the carbon spread in a thin layer in a boat. Subsequent removal of the adsorbed CO\textsubscript{2} or H\textsubscript{2}O by heating for many hours at 300°C in high vacuum is recommended. If surface oxides have formed due to adsorbed air, they may be removed by heating to red heat.

REFERENCES:

Va. H. Thiele, Forschungen und Fortschritte 10, 408 (1934); German patent 600 768.
b. U. Hofmann. German patent 752 734.

Surface Compounds of Carbon

This section is devoted to chemical compounds formed on the surface of the graphite crystal.* The internal structure of the crystal is not significantly changed by the surface compounds, which is not the case with graphite compounds.

*Chlorine is probably bound not at the surface of the graphite crystal but by hydrocarbon impurities present in the material (see DEGUSSA, Nachrichten aus Chemie und Technik, August 21, 1954).
I. OXYGEN COMPOUNDS REACTING AS ACIDS IN AQUEOUS SOLUTIONS

Preparation involves heating the carbon for many hours in a stream of O₂ at a temperature as near as possible to the ignition point, i.e., 500°C. During oxidation, the carbon must be vigorously shaken or, better still, fluidized by the O₂ stream. Since oxidation produces CO₂, which is then absorbed, it is recommended that the oxidation product be subjected to long heating at 300°C in high vacuum. It should be remembered that the oxidation is accompanied by activation with O₂.

If a highly adsorptive carbon is used, as much as 15 g. of O₂ can be taken up by 100 g. of the carbon. Under the same conditions, steam produces acid groups whose concentration may reach 700 meq. of H⁺ ions per 100 g. of the preparation. The material is tested by shaking 0.1 g. of the carbon with 100 ml. of 0.05N alcoholic KOH. The H⁺ ions can be replaced by CH₃ groups through methylation with diazomethane. Because of the acidic surface oxides, the carbon is readily wetted by water and poorly by benzene, as contrasted with carbon having no acid surface oxides. Above 500°C, O₂ is released as CO and CO₂.

II. OXYGEN COMPOUNDS REACTING AS BASES IN AQUEOUS SOLUTIONS

These compounds are always formed when carbon comes into contact with air or O₂ at room temperature. Their formation can only be avoided when contact is prevented. These basic compounds may coexist on the surface of the carbon with the acid-forming O compounds. With highly adsorptive carbon these compounds may exert, in aqueous solution, an effect equivalent to a concentration of 100 meq. of OH⁻ ions per 100 g. of carbon.

The material is tested by shaking with 0.05 N HCl. The basic surface oxides probably participate in the catalytic decomposition of H₂O₂ on carbon and when carbon is used as an oxygen electrode. Above 500°C, the O is released as CO and CO₂.

III. SULFUR COMPOUNDS

Carbon and excess S are heated for two days at 600°C in a sealed tube. The product is then washed thoroughly in a Soxhlet apparatus with CS₂, toluene and alcohol. A highly adsorptive carbon can take up as much as 30 g. of S per 100 g. of preparation. Above 500°C, the preparations release S, and as the temperature rises, CS₂ is also generated.

REFERENCES:

Regarding preparation with concentrated nitric acid, see U. Hofmann and G. Ohlerich, above.


b) Graphite Compounds

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Alkali Graphite Compounds

These may be prepared with melts or vapor of the alkali metals K, Rb and Cs. Depending on the proportions and/or the reaction temperature, the compounds resulting have the following approximate compositions: C_{8M} (1st stage), C_{24M} (2nd stage), C_{36M} (3rd stage) and C_{48M} (4th stage).

C_{8K}

The apparatus is that of Fig. 207. Section B of the approximately 22 mm I.D. glass tube is charged with about 1 g. of powdered or ground graphite which prior to use has been thoroughly heated at 900°C in high vacuum. An ampoule or glass tube containing pure K metal is introduced into A in a stream of N\textsubscript{2}, the open end facing a. After the reactor tube is sealed off at a, the K is distilled into B in high vacuum. Then an electrical heater maintained at 300°C is placed over A and B. It is desirable to rotate the tube in ground joint E after some time so that even the graphite particles adhering to the glass at the bottom may react as completely as possible. The conversion is complete when the preparation acquires a dark copper color and is homogeneous. If some blue or black particles have formed, then the heating period was too long or the temperature too high. If this is the case, some K is distilled back from 0 to B and the heating operation is repeated. After all the excess K has been distilled away from B, the material is permitted to cool. The apparatus is then filled with N\textsubscript{2} and sealed off at b and c and the tube is raised to a vertical position, so that the product is separated from the K-wetted glass wall C and collects at D. Here the attached storage tubes (only one of which is illustrated) are filled and then torch-sealed.

C_{9K}

The preparation corresponds to that for C_{8K} but the furnace is kept at 360°C. The end of the conversion is identified by the
uniformly steel-blue color of the preparation. Precautions must be taken to ensure that part of the preparation does not again turn brown by absorbing K vapor when the furnace is cooled. If this is the case, heating must be continued. If heating is continued for too long, the products are poor in K.

C₃₆M AND C₄₈M

These are prepared from a stoichiometric mixture of graphite powder or flakes and K metal by heating for 20 hours at 300 to 400°C in an evacuated, sealed tube.

Rubidium graphite and cesium graphite are prepared in similar fashion.

Analysis. After weighing, the tubes containing the substance are cut open and the contents are discharged into a preheated Erlenmeyer flask (C₉M and C₂₄M either ignite or smolder in the flask). After cooling, the graphite is boiled with water, filtered and washed. The alkali in the filtrate is determined by volumetric analysis. The dried graphite, which still contains a few percent of alkali, is repeatedly boiled (until fuming) with concentrated H₂SO₄ and then calcined. The ash content of the starting graphite is calculated from the weight of the alkali sulfate obtained.

PROPERTIES:

C₉K is dark copper-red. Larger crystals have a metallic bronze color. C₂₄K is steel blue with a metallic luster. The compounds poorer in alkali are blue-black to black. These materials are very sensitive to O₂ and moisture. They ignite in air.

Structure of C₉M: there is an expanded graphite lattice, in the c direction, with alkali layers in each vacancy of the C lattice. In C₂₄M, C₃₆M, C₄₈M, each second, third, or fourth layer vacancy of the C lattice is expanded by an intercalated alkali layer.

REFERENCES:

Alkali Ammine Graphite Compounds

Prepared from graphite and alkali metal dissolved in liquid ammonia.

About 2 g. of powdered or flake graphite and the stirring bar of a magnetic stirrer are introduced into vessel c, which has a fritted glass disc (Fig. 208). After careful drying of the apparatus and displacement of the air with pure N₂, NH₃ (liquefied over Na in vessel a) is condensed in b on the alkali metal (Li, Na, K, Rb or Cs—at least 1/30 gram-atom). Stopcock h₂ is closed and the solution is siphoned from b into c by cooling vessel c. To complete the reaction in c the contents are well stirred after removal of the cooling bath. This may cause the solution to boil (if this occurs, stopcock h₂ is opened). The solution must still be blue. If it is not, additional alkali metal must be added. Finally, stopcock h₃ is opened and the solution forced with NH₃ pressure through the frit and into another, well-cooled vessel. To wash the graphite, NH₃ is condensed in c once or twice and forced out of the vessel in the same manner as before. Then c is brought to room temperature. When no further NH₃ escapes through the pressure release valve, the apparatus is purged with N₂ and the
product is poured into tubes d, e and f, which are then sealed.

Analysis: The contents of a weighed ampoule are placed in an Erlenmeyer flask containing 50-70 ml. of ice-cold 2N H₂SO₄. The decomposed product is boiled for one half hour and the graphite is filtered off and washed. The alkali is determined as sulfate in an aliquot of the filtrate; KOH is added to another aliquot, and the NH₃ is distilled off and determined by volumetric analysis. The dried graphite is treated as described for potassium graphite compounds.

PROPERTIES:

The compound approximates C₁₂M(NH₃)₂. Very dark blue, enlarged crystals. Very sensitive to air and moisture. The K, Rb and Cs compounds can be stored indefinitely, but the Li and Na compounds decompose in a few days to amides, evolving H₂.

REFERENCE:


Graphite Oxide

Prepared by oxidation of graphite with KClO₃ in a mixture of concentrated sulfuric and nitric acids.

Graphite (10 g.), as ash-free and uniform as possible, is sus­pended in a mixture of 175 ml. of concentrated H₂SO₄ and 90 ml. of 68% HNO₃. A total of 110 g. of KClO₃ is added in small portions over a period of several days to the cooled flask. The product is repeatedly stirred with 6 to 10 liters of distilled water, then settled and decanted until the wash water is neutral to litmus. As washing progresses the blue-green particles become brown and swell increasingly as the salts are removed. At the end of the washing the settling is slow and incomplete. (Purification requires several weeks, and is shortened somewhat by use of a centrifuge.) The brown slurry is suction-filtered as much as possible, spread out to dry in air, ground and dried to constant weight in vacuum at 50°C over P₂O₅.

A light, almost white graphite oxide is obtained by washing in the dark with 5% HCl, containing ClO₂. This product contains only about 0.5% ash, but after vacuum-drying still shows a very small amount of chlorine.

Good yields of products with higher oxide contents can be achieved only when a well-crystallized graphite is used as the starting material, since otherwise the resulting oxidation products
are mostly soluble. It is advisable to use a graphite of uniform particle size, in the range 0.01-0.3 mm. The coarser the particles, the longer the time required for oxidation.

Washing of the preparation with acetic acid and ether is not recommended, as this results not only in adsorption but in acetylation of the OH groups of the graphite oxides (see References, G. Ruess).

Additional preparative methods: A faster method (Hummers and Offeman) proceeds as follows: 100 g. of finely milled graphite and 50 g. of NaNO$_3$ are stirred together in 2.3 liters of ice-cooled concentrated H$_2$SO$_4$. With vigorous stirring, 300 g. of KMnO$_4$ is added over a period of many hours. The rate of addition is governed by the particle size of the graphite. The temperature of the mixture must not exceed 20°C. The mixture is then heated to 35°C and after 30 minutes is slowly reacted with 4.6 liters of water. The reaction temperature must not exceed 70°C. The mixture is then heated to 35°C and after 30 minutes is slowly reacted with 4.6 liters of water. The hot suspension is then held at 70°C for another 15 minutes. After dilution to 14 liters, the MnO$_2$ and excess KMnO$_4$ are reduced with 3% H$_2$O$_2$. The yellow-brown suspension is filtered while still warm and washed as above.

Anodic oxidation in concentrated HNO$_3$ results in graphite with only a low degree of oxidation.

For methylation of graphite oxide with diazomethane in ether or dioxane solution, see references (Hofmann and Holst; Ruess).

SYNONYMS:

Graphite oxyhydroxide, graphitic acid.

PROPERTIES:

No definite formula. The C:O atomic ratio varies between 6:1 and 6:2.5. The ratio between C atoms and OH groups is about 4:1.

The dry material is brown to black. Very hygroscopic because of intercrystalline swelling. With careful heating to 100°C and above, CO and CO$_2$ are split off. Deflagrates on rapid heating. Hydrogen ion content (graphitic acid) available for exchange is about 600 meq./100 g. Readily reduced to graphitelike products by Sn$^{2+}$, Fe$^{2+}$, H$_2$, N$_2$H$_4$, NH$_2$OH, etc. Resistivity of the dry preparation is, depending upon the O content, between $10^3$ and $10^7$ ohm·cm.

Structure: Tetrahedrally inclined C planes with metastable bond at the O and simultaneous bonding of the OH groups.

Applications: Depolarizer in dry cells, membranes for measurement of the partial pressure of water vapor, membrane electrodes.
REFERENCES:

Carbon Monofluoride

Prepared by fluorination of graphite at 400 to 500°C.

The fluorination apparatus consists of a Cu trap, cooled with liquid nitrogen to remove impurities in the F₂ stream, and a long Cu reactor tube, about 2 cm. in diameter, screwed onto the trap. A cap, opening into a thin Cu tube 1 to 2 mm. in diameter, is screwed to the other end of the Cu tube.

About 1 g. of graphite is spread out in a thin layer in a Cu boat placed in the middle of the reactor tube. The thermocouple is insulated from the tube wall by a thin layer of asbestos. A thicker asbestos layer protects it from contact with the furnace windings. The hot junction is, of course, exposed.

The graphite is thoroughly heated at 800 to 900°C in high vacuum for an hour or two immediately before the fluorination. Only after complete cooling in high vacuum is N₂ is admitted.

A slow F₂ stream (3-6 liters/hr) is passed through the apparatus and over the graphite at room temperature for 20 minutes before the start of the fluorination proper. Only then is the furnace turned on. The reaction starts between 420 and 500°C, but the initial conversion proceeds quietly within a narrow range of only about 30°. The temperature at the onset of the reaction is significantly dependent upon the size of the graphite crystals and the HF and O₂ content of the F₂ stream. With very finely powdered graphite of <0.01 mm. particle size and with impure F₂, combustion to volatile carbon fluorides may occur even at 400°C. Preparations that are already well fluorinated will tolerate temperatures as high as 520°C toward the end of the reaction. Deflagration always occurs above 550°C.

The progress of the reaction is followed by cooling the graphite in a stream of F₂ and weighing. If no weight gain occurs within an hour, the reaction may be presumed to be over. The total fluorination time is four to seven hours.

The yield, based on the graphite, is almost quantitative, but when fluorination is continued for longer periods, slight losses,
due to combustion to volatile carbon fluorides, are sustained. The fluorine content computed from the weight gain is usually 1% less than the real content.

Analytical determination of F is accomplished by decomposition with metallic Na in a sealed iron tube at 900°C. The Na is removed with alcohol, and the F precipitated as PbFCl after filtering off the C.

SYNONYM:

Graphite fluoride.

PROPERTIES:

Depending on experimental conditions, the fluorination products have compositions varying between CF\textsubscript{0.88} and CF\textsubscript{0.99}. When the F content is low, the preparation is gray black, while at very high F contents it is silver white. Depending upon F content, the densities vary between 2.78 and 2.50 (in xylene). The resistivity is greater than 10\textsuperscript{8} ohm · cm.

The preparations are not wetted by water and are neutral to acids and bases. Hydrogen has no effect below 400°C. Reduced to graphite on boiling with Zn dust and glacial acetic acid. Above 400°C thermal decomposition to volatile carbon fluorides occurs. When heating is rapid and the temperatures high, this is accompanied by deflagration and flame.

Structure: Tetrahedrally inclined C planes with F atoms bonded above and below the C planes.

REFERENCES:

O. Ruff, O. Brettschneider and E. Ebert, Z. anorg. allg. Chem. 217, 1 (1934).

Tetracarbon Monofluoride

Prepared by fluorination of graphite at room temperature in the presence of HF.

A stream of F\textsubscript{2} at 4-5 liters/hr. is passed through a copper wash flask held at 0°C and filled with anhydrous HF, and then through an attached Cu tube (about 2 cm. in diameter). A Cu boat containing a thin layer of about 1 g. of graphite is placed in the tube. The end of the tube is closed with a screw-on cap having a narrow opening. The reaction is finished after one or two hours,
as shown by the constant weight of the product. To remove excess HF, the preparation is washed with dilute base, water and alcohol and dried to room temperature over soda-lime. The yield is quantitative.

Quantitative determination of F is carried out in the same manner as with carbon monofluoride.

**PROPERTIES:**

The composition lies within the range C$_3$F to C$_4$F. The color of the preparation is velvety black, sometimes somewhat bluish, d (under xylene) 2.05-2.09. Resistivity 2-4 ohm · cm. at 750 kg/cm$^2$.

Stable to acids, bases and the common organic reagents. Slowly decomposes when heated for a long period above 100°C. Deflagrates when rapidly heated over a flame, forming sootlike flakes.

*Structure:* Flat C layers as in graphite, with F atoms bonded above and below the C layers.

**REFERENCE:**


**Graphite Salts**

Prepared by oxidation of graphite in the presence of anhydrous acids.

**GRAPHITE BISULFATE**

An agitated suspension of about 1 g. of graphite (coarse or finely crystalline) in 10 ml. of concentrated H$_2$SO$_4$ is mixed with a solution of CrO$_3$ or K$_2$Cr$_2$O$_7$ in concentrated H$_2$SO$_4$. At least 3 meq. of active oxygen (100 mg. of CrO$_3$ per g. of C) is required for complete oxidation of the graphite. After 15 minutes the graphite is uniformly dark blue and can be suction-filtered through a glass frit and washed with H$_2$SO$_4$. Removal of the adhering H$_2$SO$_4$ may be accomplished only by very long washing with sirupy pyrophosphoric acid or quick washing with ice-cold dimethyl sulfate. The reaction is virtually quantitative when coarse crystalline graphite is used, but when fine crystalline carbon is employed, brown, colloidal oxidation products also appear.

When oxidation is incomplete or the blue bisulfate is reduced with Fe (II), Sn (II) or with graphite itself, the product is less highly oxidized and the color is no longer blue.

The analytical composition may be determined from the quantity of oxidants consumed in preparation, from the oxidizing effect
II. CARBON

upon reducing agents, or by determination of the sulfate content after washing with $H_2P_2O_5$ or $(CH_3)_2SO_4$.

**Additional preparative methods:** The graphite may also be oxidized with $S_2O_5^{2-}$, $PbO_2$, $HIO_3$, $HIO_4$, $Mn(III)$ and $Mn(IV)$ compounds, as well as anodically.

**PROPERTIES:**

The composition of the blue compound corresponds (in acid) to about $C_2^+H_2SO_4 \cdot 2H_2SO_4$.

The product is as crystalline as the initial graphite, but swollen and very dark blue. It may be stored only under concentrated acid. Decomposed immediately by water, humid air, alcohol, ether, acetone and benzene.

**STRUCTURE:**

In the blue bisulfate, layers of acid anions and molecules are intercalated between the C planes. In the less oxidized black products, acid layers are intercalated in regular sequence in each second, third, fourth, etc., layer vacancy.

**GRAPHITE NITRATE, GRAPHITE PERCHLORATE**

Prepared by washing graphite bisulfate (see above) with fuming nitric acid (d 1.52) or with 70% $HCIO_4$, respectively, until the filtrate is free of sulfate ions, or by oxidation of graphite in the corresponding acids, $N_2O_5$ being present in the case of nitrate and $CrO_3$ in the case of perchlorate. The conversion of the bisulfate is reversible.

Properties and structure correspond to those of graphite bisulfate.

For other salt-type graphite compounds with $HF$, $H_2SeO_4$, $H_3PO_4$ and $H_3AsO_3$, see the references.

**REFERENCES:**


**Bromine Graphite**

Prepared by action of bromine upon graphite.

Coarse or fine crystalline graphite, in a weighing bottle, is allowed to stand over bromine in a desiccator for many hours at room temperature. The maximum weight gain of the graphite is 0.82-0.84 g. per g. of C.
PROPERTIES:

The composition corresponds to an atomic ratio C:Br of about 8:1.

Black to blue-gray crystals, as in the starting graphite, but enlarged. Most of the Br₂ taken up is desorbed in air and can be washed out with water.

*Structure:* Graphite lattice with a bromine layer in every second layer vacancy.

REFERENCE:


**Metal Halide Graphite Compounds**

Prepared from graphite and anhydrous metal halides, e.g., FeCl₃, AlCl₃, GaCl₃, InCl₃, MoCl₅, UCl₅, etc. With the exception of FeCl₃, these metal halides can be intercalated only in the presence of free chlorine.

A) IRON (III) CHLORIDE GRAPHITE

A glass tube of about 2 cm. I.D. is used. At least 5 g. of anhydrous FeCl₃ is sublimed onto 2 g. of coarse or fine crystalline graphite. The tube is sealed off on both sides and heated for 24 hours in an electric tubular furnace at a constant temperature of 200-300°C. One end of the tube is then withdrawn from the furnace, and the heating is continued at the same temperature until no further uptake of the desublimed FeCl₃ can be observed.

PROPERTIES:

Black, highly enlarged crystals. The FeCl₃ content depends upon the temperature of desublimation and is in the range of 60-70% FeCl₃. When heating is rapid, there is pronounced swelling with elimination of FeCl₃. The crystals release FeCl₃ in water, dilute acids, alcohol or benzene. Depending on the size of the crystals, the washed preparations contain 52-56% FeCl₃.

B) ALUMINUM CHLORIDE GRAPHITE

Preparation is similar to that presented above under (A). About 3-4 g. of AlCl₃ is sublimed in a stream of dry Cl₂ onto 1 g. of graphite. The sealed reaction tube (capacity about 40 cm³) must
be well filled with Cl₂. The heating of the reaction mixture and subliming of the excess AlCl₃ are carried out at 150 to 200°C.

**PROPERTIES:**

Very dark blue, lustrous, highly enlarged crystals; releases AlCl₃ and Cl₂ when heated above 260°C; very hygroscopic. Water and organic solvents dissolve out much of the intercalated AlCl₃. Precipitates iodine when added to KI solution. The compound corresponds approximately to C⁺⁺⁺⁺AlCl⁻⁻⁻⁻ · 2AlCl₃.

Structure of A and B. Graphite lattice expanded in the c direction with a layer of metal halide in each layer vacancy.

**REFERENCES:**


c) **Volatile Carbon Compounds**

O. GLEMSER

**Carbon Monoxide**

CO

1. **FROM FORMIC ACID**

\[ \text{HCOOH} = \text{CO} + \text{H}_2\text{O} \]

46.0 22.4 1

A gas generator (one-liter round-bottom flask with ground glass dropping funnel and gas outlet tube) two-thirds full of concentrated phosphoric acid is heated to 80°C in a water bath. Formic acid is then added slowly, drop-by-drop. Removal of impurities (CO₂, air, acid vapors, water vapor) is effected by passing the gas successively through 50% KOH solution and an alkaline solution of Na₂S₂O₄ (25 g. of Na₂S₂O₄ in 125 ml. of H₂O, plus by 20 ml. of 70% KOH) and over KOH, CaCl₂ and P₂O₅.

Traces of O₂ may also be removed with a glowing carbon filament [K. Clusius and W. Teske. Z. phys. Chem. (B) 6, 135 (1929)]. Larger quantities of oxygen are removed in a purification train consisting of three wash bottles in series, two of which contain 100 g. of slightly amalgamated Zn and 100 ml. of 0.1M VOSO₄.
O. Glemser

solution, while the third contains 100 ml. of H$_2$O [L. Meites and T. Meites. Anal. Chem. 20, 984 (1948)].

Very pure CO is obtained by liquefaction of the gas and double fractionation (impurities <10$^{-3}$ mole%).

II. FROM OXALIC ACID

\[ \text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O} \rightarrow \text{CO} + \text{CO}_2 + 3\text{H}_2\text{O} \]

A mixture of 100 g. of oxalic acid dihydrate and 275 ml. of concentrated H$_2$SO$_4$ is heated carefully in a round-bottom flask until the onset of gas generation, which must not be allowed to proceed too vigorously. The CO$_2$, formed in equal amounts with the CO, is absorbed in two wash bottles each containing 100 ml. of 50% KOH solution. Purification is the same as in method I.

Other preparative methods: III. From formic acid or barium formate and phosphoric acid [J. G. Thompson, Ind. Eng. Chem. 21, 389 (1929)]. This method is particularly suitable for a continuous process and gives a 92% yield.


V. By dry heating of a mixture of CaC$_2$O$_4$ and CaO [A. Klemenc, Die Behandlung und Reindarstellung von Gasen [Treatment and Purification of Gases], Vienna, 1948, p. 159].

Procedures IV and V are not as satisfactory as I.

VI. Small amounts of very pure gas may be prepared by thermal decomposition of Ni(CO)$_4$ [A. Mittasch. Z. phys. Chem. 40, 1 (1902); C. E. H. Bawn. Trans. Faraday Soc. 31, 440 (1935)].

VII. From CaCO$_3$ powder and Zn dust at 700 to 750°C; very pure gas results [S. Weinhouse. J. Amer. Chem. Soc. 70, 442 (1948)].

Purification of tank CO: Possible impurities: CO$_2$, O$_2$, H$_2$, CH$_4$, N$_2$, Fe(CO)$_5$. The gas is passed slowly through a tube filled with reduced copper wire and heated to 600°C; this removes O$_2$ and Fe(CO)$_5$. The activated Cu-filled tube of Meyer and Ronge (see section on Nitrogen, p. 458) may also be used. The CO then flows through a tower filled with moist KOH to absorb the CO$_2$. Should further purification (particularly removal of H$_2$) be necessary, the CO must be liquefied and fractionally distilled.

PROPERTIES:

Formaldehyde, colorless and odorless gas. M.p. -205.1°C, b.p. -191.5°C; crit. t. -140.2°C; crit. p. 34.5 atm.; triple pt. p. 115.0 mm. Burns with a blue flame; ignition point 700°C in the air; lower explosion limit in moist air: 12.5% CO. At elevated temperatures, decomposes into CO$_2$ and C. Solubility
in \( \text{H}_2\text{O} \) (0°C) 3.3, (20°C) 2.3 vols. of CO/100 g. \( \text{H}_2\text{O} \). About seven times as soluble in methyl and ethyl alcohols as in \( \text{H}_2\text{O} \). Readily soluble in acetic acid, \( \text{CHCl}_3 \) and ethyl acetate. \( d \) (liq., -195°C) 0.814; \( d \) (gas, 0°C) 1.250 g./liter. Heat of formation -26.39 kcal./mole.

REFERENCES:


**Carbon Dioxide**

\( \text{CO}_2 \)

PURIFICATION OF TANK \( \text{CO}_2 \)

Possible impurities: water vapor, CO, \( \text{O}_2 \) and \( \text{N}_2 \), sometimes accompanied by traces of \( \text{H}_2\text{S} \) and \( \text{SO}_2 \).

I. Moderately Pure \( \text{CO}_2 \): The gas is passed sequentially through the following vessels: 1) two wash bottles with \( \text{Cr(II)} \) acetate solution or \( \text{VOSO}_4 \) solution to remove the bulk of the \( \text{O}_2 \) (also see \( \text{CO} \), method I); 2) a U tube containing small pieces of \( \text{KHCO}_3 \) (for removal of acid vapors); 3) a U tube with pumice impregnated with \( \text{CuSO}_4 \) solution, or a wash bottle filled with \( \text{1M K}_2\text{MnO}_4 \) solution or \( \text{1M K}_2\text{Cr}_2\text{O}_7 \) solution (removal of \( \text{H}_2\text{S} \)); 4) a wash bottle with concentrated sulfuric acid (for drying); and 5) a Meyer and Ronge tube filled with activated \( \text{Cu} \) and \( \text{Cu}_2\text{O} \) heated to 200°C (see description of the purification of \( \text{N}_2 \), p. 458) for removal of the last traces of \( \text{O}_2 \) and \( \text{CO} \). Instead of 3 and 4, R. Weber recommends [Angew. Chem. 65, 136 (1953)] that organic compounds and \( \text{H}_2\text{S} \) be removed by passing the gas through a mixture of 100 volumes of \( \text{H}_2\text{SO}_4 \) (d 1.84) and 3.3 volumes of aqueous formaldehyde (40 vol. %). If a given impurity is not present, the corresponding purification step may be omitted.

II. Purer \( \text{CO}_2 \): The gas is passed through saturated \( \text{CuSO}_4 \) through \( \text{KHCO}_3 \) solution, and finally through a fractionator (Klemenc and Bankowski). This apparatus is a portion of the equipment presented in Fig. 153 (p. 345) for the preparation of very pure \( \text{H}_2\text{S} \). To fractionate \( \text{CO}_2 \) one employs only the section to the right of wash bottle 4, consisting of eight well-cooled U tubes and two low-temperature traps. Immediately before the last condensation trap \( A_2 \), a mercury manometer tube is inserted on a side tube. The \( \text{CO}_2 \) is frozen out in \( A_1 \) after passing through the first four
U tubes, cooled to the temperatures indicated in the figure. When $A_1$ is sufficiently full, stopcock $a$ is opened, the tube is sealed off at point $c$, and the remaining apparatus is evacuated to a low pressure. After the remaining four U tubes have been cooled to $-78^\circ$C (Dry Ice-acetone), the liquid nitrogen is removed from around $A_1$, the first fraction of gas is siphoned off, and condensation vessel $A_2$ is immersed in liquid nitrogen. The middle fraction is collected in $A_2$, the residue being left in $A_1$. The material is sublimed twice from $A_2$ and the purity of the gas is checked by its vapor pressure at various temperatures. The gas is stored in 25-liter glass flasks which have been degassed by heating in high vacuum at $350^\circ$C for many hours.

SYNONYM:

Carbonic acid anhydride.

PROPERTIES:

Formula weight 44.01. Colorless, odorless gas. Subl. t., $-78.48^\circ$C (atmospheric pressure); m.p. $-56.7^\circ$C (5 atm.); crit. t. 31.3°C; crit. p. 72.9 atm.; crit. d 0.464; triple pt. $-56.6^\circ$C at 5.11 atm. Vapor pressure ($-120^\circ$C) 10.5; ($-100^\circ$C) 104.2; ($-82^\circ$C) 569.1 mm.

Solubility in $H_2O$. (0°C) 171; (20°C) 88; (60°C) 36 ml. of $CO_2/100$ g. of $H_2O$.

d (vapor, 0°C) 1.977 g./liter; d (liq., 0°C) 0.914 (34.4 atm.); d (solid, $-56.6^\circ$C) 1.512. Heat of formation $-94.05$ kcal./mole.

REFERENCES:

I. L. Moser. Z. anorg. allg. Chem. 110, 125 (1921).
II. A. Klemenc and O. Bankowski. Z. anorg. allg. Chem. 208, 348 (1932); 209, 225 (1932).

Tricarbon Dioxide

$C_3O_2$

I. THERMAL DECOMPOSITION OF MALONIC ACID IN THE PRESENCE OF $P_2O_5$

$$C_3H_4O_4 = C_3O_2 + 2 H_2O$$

114.1 68.0

Flask $a$ of the apparatus illustrated in Fig. 209 is charged with 20 g. of malonic acid, 40 g. of calcined sand and 200 g. of fresh, uncaked and well mixed $P_2O_5$. The system is evacuated to 0.1 mm.
stopcock \( h \) is closed, and the apparatus is left to stand for some hours to complete the drying and to test for leaks. The pump is then started, stopcock \( m \) is opened once again, \( d \) is cooled with liquid nitrogen and \( a \) is heated on an oil bath to 140°C. At this temperature, decomposition is complete within about an hour and impure \( \text{C}_3\text{O}_2 \) condenses in \( d \). Now the oil bath is removed, \( m \) is closed, the pump is stopped, dry air is introduced at \( h \), and \( a \) is removed from the system and sealed off at \( c \). The system is again evacuated, \( m \) is closed, and the contents of \( d \) are slowly distilled into trap \( h \), cooled with liquid nitrogen. Plugging of \( h \) should not be allowed to occur. Acetic acid and other impurities are absorbed in the lime tower and the material is fractionated in high vacuum with stopcock \( f \) closed. This is done by placing \( h \) in an alcohol bath \((-110°C \text{ to } -115°C)\), while \( l \) is cooled with liquid nitrogen, stopcock \( t \) is closed, and the condensate in \( h \) is melted. Then \( h \) is again immersed in the alcohol bath, \( t \) is opened, and distillation into \( l \) proceeds. Pressure changes are followed on the manometer. When the manometer pressure is still but a few tenths of a millimeter, the vapor pressure is determined at 0°C and compared with that of the pure gas (573.5 mm.).

Separation of the \( \text{C}_3\text{O}_2\text{-CO}_2 \) mixture (\( \text{CO}_2 \) is a product of the side reaction \( \text{C}_3\text{H}_4\text{O}_4 = \text{CH}_3\text{COOH} + \text{CO}_2 \)) is difficult. Therefore, when the solid phase (\( \text{CO}_2 \)) has disappeared, it is advisable to reduce the bath temperature to \(-125°C \text{ or } -130°C\) for completion of the separation. Fractionation takes about 15 hours (A. Klemenc, loc. cit.).

Fig. 209. Preparation of tricarbon dioxide from malonic acid. \( a \) one-liter reaction flask; \( b \) rubber stoppers, lightly greased; \( c \) connecting tube, 10 mm. I.D. \( d \), \( h \) and \( l \) traps; \( e \) drying tower containing pea-sized, freshly calcined pieces of \( \text{CaCO}_3 \); \( f \) 800-mm.-long manometer tube.
A. Klemenc, R. Wechsberg, and G. Wagner have suggested inserting before the lime tower a tube filled with glass wool to retain the P₂O₅, condensing the reaction products ahead of stopcock γ in a liquid-nitrogen-cooled vessel, and finally distilling once again into λ via a tube filled with glass wool and a lime tower.

The yield of C₃O₂ is 2.94 g. (22%). Determination of yield: C₃O₂ (alone or mixed with other gases) is passed through a solution of aniline in xylene. The malononilide formed is virtually insoluble in xylene and precipitates as colorless crystals, m.p. 223°C.

Additional preparative method: Thermal decomposition of diacetyltartaric anhydride (Klemenc et al.). The yield is better, but the C₃O₂ contains ketene, which cannot be completely separated.

SYNONYM:
Carbon suboxide.

PROPERTIES:

Formula weight 68.03. Colorless, highly refractive liquid or colorless, poisonous gas of stifling odor. M.p. -112.5°C, b.p. 67°C; d°C 1.114; vapor pressure (0°C) 573.5 mm. (corr.).

Attacks hydrocarbon but not silicone grease. The gas can be stored at pressures of up to 100 mm., but it is common even at these pressures for polymerization to occur, giving a red, water-soluble product. This invariably occurs at higher pressures or in the liquid state. The presence of P₂O₅ facilitates polymerization. Decomposes when passed through heated glass tubes, forming a mirror surface.

Soluble in CS₂ and xylene. Quantitatively decomposed by water (within one hour) to malonic acid. Forms malonamide with ammonia.

Heat of formation 47.4 kcal./mole.

REFERENCES:

**Carbonyl Chloride**

**COCl₂**

**PURIFICATION OF TANK COCl₂**

Possible impurities: CO₂, CO, air, HCl and H₂O, total approximately 1%.
I. Small quantities: The COCl$_2$ is removed from the tank and condensed with an ice-salt mixture. To remove the volatile portion, about a fifth of the condensate is permitted to evaporate, and the residue is fractionated in high vacuum until all fractions have the same vapor pressure. The pure gas has a vapor pressure (0°C) of 556.5 mm.

II. Larger quantities, moderate purity requirements: Carbonyl chloride is condensed in a flask with sealed-in gas inlet tube and cooled with an ice-salt mixture. A water-cooled bulb-type reflux condenser is placed on top of the flask. The condenser is connected to a Hempel gas burette filled with 7-8°C water. The burette is joined to a downward condenser (cooled with ice-salt), which in turn is connected to a receiver. The cooling mixture is removed from around the flask, about a fifth of the liquid is permitted to evaporate, and the receiver is cooled, thus condensing the COCl$_2$. The impurity content is less than 0.4%.

Analytical determination: Carbonyl chloride is shaken with an aqueous aniline solution and the diphenylurea product is determined gravimetrically or, after conversion to NH$_3$, colorimetrically.

SYNONYM:

Phosgene.

PROPERTIES:

Formula weight 98.92. Colorless, highly poisonous gas of stifling odor reminiscent of rotten hay.

M.p. $-128°C$, b.p. 7.5°C; crit. t. 181.7°C; crit. p. 55.3 atm; vapor pressure (0°C) 556.5 mm.

Strongly attacks stopcock grease; may be stored in glass vessels at 0°C. Very slightly soluble in cold water. Hot water hydrolyzes it readily to HCl and CO$_2$. Readily soluble in benzene, toluene, glacial acetic acid, CCl$_4$ and hexamethylenetetramine, as well as in AsCl$_3$ and S$_2$Cl$_2$. Decomposes to CO and Cl$_2$ on heating (503°C, 50%; 800°C, 100%).

d (liq., 0°C) 1.436; vapor d (18.6°C) 1.392 g./liter. Heat of formation $-53.3$ kcal./mole.

REFERENCES:

I. A. Stock and E. Wustrow. Z. anorg. allg. Chem. 147, 245 (1925).
Carbon Disulfide

CS₂

PURIFICATION OF COMMERCIAL MATERIAL

Possible impurities: dissolved S, H₂S, H₂SO₃, H₂SO₄, organic sulfur compounds, H₂O.

Half a liter of CS₂ is shaken for an hour with 100-200 g. of Hg and some P₂O₅; the mixture is filtered and the filtrate is distilled in a column, in the dark if possible. The low-boiling fraction and the high-boiling fraction (recognizable by the yellow color of the residue in the distillation flask) are discarded. The bulk of the distillate is shaken once again with Hg and P₂O₅ and fractionally distilled, and the first and last cuts are discarded. These steps are repeated until no black HgS is formed. If a very pure product is desired, distillation in high vacuum is necessary. If the only impurity is H₂S, a single fractionation is sufficient.

Testing for purity: Residue: When concentrated by evaporation on the water bath, 50 ml. of CS₂ should leave no residue. Dissolved S: When thoroughly agitated with dry Hg in a dry vessel, the Hg must not acquire a dark coating. H₂S: No brown tint should appear on shaking with lead carbonate. For H₂SO₃ and H₂SO₄: If H₂O shaken with the CS₂ gives an acid reaction, either H₂SO₃ or H₂SO₄ is present.

SYNONYMS:
Carbon bisulfide, dithiocarbonic anhydride.

PROPERTIES:

Formula weight 76.13. The liquid is water clear and highly refractive, with an odor of ether. F.p. -111.6°C, m.p. -108.6°C, b.p. 46.25°C; crit. t. 273.05°C; n⁰ 1.6295; vapor pressure (0°C) 127.3 mm.

Decomposes on standing for a long time, especially in light. Decomposition is recognized by the unpleasant odor. Burns with a blue flame to CO₂ and SO₂; ignition point 236°C.
Slightly soluble in H₂O; soluble in ethyl alcohol, benzene, ether, and essential and aliphatic oils.

d⁰ 1.293, d₂⁰ 1.262. Heat of formation 21.0 kcal./mole.

REFERENCES:
Tricarbon Disulfide
$C_3S_2$

Prepared by reaction of Zn with liquid CS$_2$ in an electric arc:

$$3 \text{CS}_2 + 4 \text{Zn} \rightarrow \text{C}_3\text{S}_2 + 4 \text{ZnS}$$

Chemically pure CS$_2$ (1500 ml.), previously agitated with Hg and P$_2$O$_5$ and then fractionated, is placed in a two-liter round-bottom flask immersed in ice up to the neck. A three-hole stopper—for CO$_2$ inlet tube and for the two 6-mm. brass wires of the electrode holder—is fitted loosely into the flask opening. The cylindrical zinc anode (15-20 mm. long, 6 mm. diameter) is supported on a brass wire with two right-angle bends and is placed just above the bottom of the flask. Opposite it is the graphite cathode (80 mm. long, 12 mm. diameter), mounted on the other brass wire. The upper end of this brass wire is connected to the mechanical adjustment device of a differential arc torch and moved downward to prevent interruption of the arc due to vaporization of the electrodes. A stream of CO$_2$ is now introduced and the two electrodes are brought together. The current is turned on and the electrodes are separated to strike the arc. The current should be 4-5 amp. with 20-25 volts across the terminals. The CS$_2$ soon becomes opaque due to finely divided carbon.

The reaction product, a red-brown liquid of stifling odor, is filtered, the filter residue washed with some CS$_2$ and the filtrate shaken with 200 g. of Hg and some P$_2$O$_5$. After filtering, four fifths of the liquid is vaporized on a water bath and then evacuated at room temperature with a pump until all the CS$_2$ is expelled. The remaining red fluid is distilled in high vacuum into a receiver cooled to $-40^\circ\text{C}$, in which the C$_3$S$_2$ condenses as a yellowish red solid substance of high purity. The yield is 800-850 mg. of C$_3$S$_2$ (50% of theoretical) when the arc is on for five hours.

**Determination of C$_3$S$_2$:** The CS$_2$ solution, concentrated to about 100 ml., is completely vacuum distilled into a cold flask, and the condensate, consisting solely of CS$_2$ and C$_3$S$_2$, is treated with excess Br$_2$, allowed to stand for a few hours, and evaporated in a stream of dry air. The residue is yellow C$_3$S$_2$Br$_6$, stable in air.

**SYNONYM:**
Carbon subsulfide.

**PROPERTIES:**

Bright red, highly refractive liquid with a strong odor that affects the mucous membranes. M.p. $-0.5^\circ\text{C}$; vapor pressure ($50^\circ\text{C}$) 8 mm., ($90^\circ\text{C}$) 48 mm.
Decomposes above 90°C. Solutions of $\text{C}_3\text{S}_2$ in $\text{CS}_2$ containing more than 1% $\text{C}_3\text{S}_2$ are not stable and gradually precipitate black polymerization products. Sunlight has the same effect, even in dilute solutions. At 160°C, pure $\text{C}_3\text{S}_2$ yields a solid black product. With aniline, $\text{C}_3\text{S}_2$ forms thiomalonanilide.

REFERENCES:
A. Stock and P. Praetorius. Ber. dtsch. chem. Ges. 45, 3568 (1912);

Carbonyl Sulfide

\[
\text{COS}
\]

I. \[\text{CO} + \text{S} = \text{COS}\]

Carbon monoxide is admitted into the apparatus shown in Fig. 210 to expel the air and pure S in $\sigma$ is heated to the boiling point. The side tube $\delta$ is heated to 350°C by an electric furnace. The resultant COS flows, together with the CO, through vessels $e$, $f$ and $\sigma$, and is condensed in the trap $\lambda$. Tube $\sigma_1$ is kept at $-20^\circ$C; $\sigma_2$ and $\sigma_3$ are at $-60^\circ$C. The condensed gas still contains some 2% of impurities, which are removed by high-vacuum distillation.

The gas rate must be so regulated that excessive quantities of S dust do not reach the vicinity of the cooled rubber stopper, or the tube will readily be plugged. The optimum flow rate is approximately eight liters/hour, in which case the yield is 75%.

II. \[2\text{NH}_4\text{NCS} + 2\text{H}_2\text{SO}_4 + 2\text{H}_2\text{O} = 2(\text{NH})_2\text{SO}_4 + 2\text{COS}\]

A cooled mixture of 2080 g. of concentrated $\text{H}_2\text{SO}_4$ and 1000 g. of $\text{H}_2\text{O}$ is placed in a round-bottom flask provided with a gas outlet tube and immersed in a water bath. Saturated $\text{NH}_4\text{NCS}$ solution (200 ml.) is added from a dropping funnel. The water bath is now heated to about 30°C, resulting in a vigorous generation of gas. The solution is shaken back and forth. The evolved gas (impurities consist of $\text{NH}_3$, $\text{H}_2\text{S}$, $\text{CS}_2$, $\text{CO}_2$, $\text{HCN}$, $\text{H}_2\text{O}$, etc.) passes through a ten-bulb tube filled with 33% NaOH. It is then dried in two lime-filled drying towers and in another filled with CaCl$_2$ and is finally condensed in a U tube kept at $-70^\circ$C. The yield is 75%, based on HNCS.

The gas is separated from the admixed CO$_2$ (0.1 vol.%) by high-vacuum fractionation. Qualitative test for CO$_2$ in COS: reaction
with Ba(OH)$_2$ solution. Pure COS shows no discernible initial reaction.

**PROPERTIES:**

Formula weight 60.07. Colorless, poisonous gas with a mild odor. M.p. —138.2°C, b.p. —50.2°C; vapor pressure (—75°C) 210 mm. Mixtures of air and COS are explosive when they contain between 11.9 and 26.5 vol.% COS. At 300°C, COS decomposes to CO and S. In air, burns with a blue flame to give CO$_2$ and SO$_2$. May be stored when dry; hydrolyzed by water and water vapor. Water reacts slowly, yielding CO$_2$ and H$_2$S. Absorbed and rapidly decomposed by KOH. Solubility (20°C) 0.54 ml. of COS/g. of H$_2$O; (22°C) 8 ml. of COS/ml. of alcohol; (22°C) 15 ml. of COS/ml. of toluene. Solubility in CS$_2$ is even greater. d (liq., —87°C) 1.24; vapor d (0°C) 1.073 g./liter. Heat of formation —33.9 kcal./mole.

**REFERENCES:**


**Carbonyl Selenide**

**COSe**

I. $\text{CO} + \text{Se} = \text{COSe}$

Carbon monoxide, generated from formic and phosphoric acids, is passed through 50% KOH solution, dried with KOH, CaCl$_2$ and
P₂O₅, and passed through a flow meter into a Vycor or ceramic reaction tube in which Se is heated to 780°C. Because of the Se dust, the apparatus shown in Fig. 210 is used. However, section d is not filled with pumice and is not heated. The gas then passes through the various traps, which are cooled with ice, Dry Ice and liquid nitrogen. The condensate from the trap cooled with liquid nitrogen is fractionated in high vacuum. The yield at 15 liters of CO/hour is about 9.8 vol.% COSe.

Determination of yield: The gas mixture is introduced into a glass bulb of known volume and hydrolyzed for 15 minutes with 2N NaOH; air is then admitted while the solution is heated and the precipitated Se is weighed after washing with water and methyl alcohol and drying at 105°C.

Analysis: A weighed amount of COSe is absorbed in KOBr solution. At the end of the reaction, concentrated hydrochloric acid is added until the solution is mildly acidic. It is then reduced to elemental Se at 70°C by addition of hydrazine sulfate. After cooling, the material is filtered, washed with water and methanol, dried at 105°C and reweighed.

Other preparative method: Al₂Se₃ + 3 COCl₂ = 2 AlCl₃ + 3 COSe (O. Glemser and T. Risler).

Properties:
Formula weight 106.97. Colorless, very poisonous gas, with a characteristic odor reminiscent of H₂Se. M.p. —124.4°C, b.p. —21.7°C; vapor pressure (—31.4°C) 498.7 mm.; crit. t. 121.1°C. Hydrolyzes with water or water vapor, precipitating red Se. Acids act slowly, while oxidizing acids and H₂O₂ oxidize it to SeO²⁻. Alkaline solutions hydrolyze it rapidly and quantitatively to Se²⁻ and CO³⁻. Decomposed into CO and Se by porous substances such as activated charcoal. Very soluble in COCl₂.

d (liq., 41°C) 1.812.

References:

Carbon Diselenide

CSe₂

I. CH₂Cl₂ + 2 Se = CSe₂ + 2 HCl

As shown in Fig. 211, a dry stream of N₂ is saturated with CH₂Cl₂ vapor, and the gas mixture is introduced into a Vycor
flask in which Se is heated to 550–600°C. The crude product precipitates in the receiver, equipped with a Liebig condenser. The cooling by the condenser is stopped and the liquid is forced with steam into a cooled flask, separated from the H₂O and dried over CaCl₂. It is then distilled at 46°C and 50 mm. in a fractionating column (30 cm. long).

A deposit of C forms in the reaction zone. This may inhibit the reaction under certain conditions. This deposit can be prevented by adding the Se in smaller portions.

The yield is greater if the reaction vessel employed is of the same type as that used to produce COS (Fig. 210) and if the inclined tube, which is empty in this experiment, is heated to 200°C with an electric furnace. The entraining of red Se dust by the gas stream is thus greatly decreased. The yield is 52%, based on the Se charged.

\[
\text{II. } \text{C}_4\text{Cl}_4 + 2\text{H}_2\text{Se} = \text{CSe}_2 + 4\text{HCl}
\]

A stream of oxygen-free N₂ is passed into a wash bottle equipped with a glass frit and filled with H₂O. The bottle is held at 64°C (p = 180 mm.) and the gas mixture is run, without condensing the vapor, through a tube filled with finely divided Al₂Se₃ and pumice. The outlet mixture of N₂ and H₂Se gases is dried with CaCl₂. A stream of N₂ is saturated with CCl₄ in the same manner in a second wash bottle (20°C, 90 mm.). The rate of the two gas streams is six liters/hour. The two streams are combined in a 500-mm.-long Pyrex tube heated to 500°C, and then passed

**Fig. 211. Preparation of carbon diselenide.**
through two traps held at $-70^\circ$C (Dry Ice-acetone). At the end of
the reaction, $H_2O$ is added to the condensate, and $CCl_4$ and $CSe_2$ are
distilled from the higher boiling impurities (e.g., selenium chlo-
rides). The distillate is fractionated in an efficient column, first
at atmospheric pressure, then at $125$ mm. At $68^\circ$C virtually pure
$CSe_2$ distills over. This is distilled further.

**SYNONYM:**

Carbon selenide.

**PROPERTIES:**

Golden yellow, highly refractive liquid; odor of rotten radishes.
M.p. $-45.5^\circ$C, b.p. 125-126$^\circ$C (760 mm.); vapor pressure ($0^\circ$C)
4.7 mm.; $n_D^{20} 1.845$.

Very sensitive to light; turns brown and finally black on standing.
Burns with difficulty. When heated in a sealed tube to $150^\circ$C,
solidifies to a black mass (polymerizes?). Insoluble in $H_2O$; dis-
solves, yielding a yellow liquid, in $CS_2$, $CCl_4$, ether, benzene,
nitrobenzene, dioxane, ethyl acetate and acetone. Slightly soluble
in glacial acetic acid and alcohol, decomposing these rapidly;
pyridine behaves in the same manner. Dissolves copious quantities
of flowers of sulfur, but red Se hardly at all. Decomposed on
boiling with concentrated nitric acid. Decomposed by concentrated
$NaOH$ to a marked degree, but only on heating. $d_2^0 2.682$. Heat of
formation 34 kcal./mole.

**REFERENCES:**

(London) 1947, 1080.
II. H. G. Grimm and H. Metzger. Ber. dtsch. chem. Ges. 69,
1356 (1936).

**Hydrogen Cyanide**

$HCN$

I. $2NaCN + H_2SO_4 = Na_2SO_4 + 2HCN$

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The long-neck, round-bottom flask $a$ of the apparatus in Fig.
212, containing 1 kg. of concentrated sulfuric acid, 400 ml. of $H_2O$,
20 g. of $FeSO_4$ and a few boiling stones, is heated on a water bath
to $90^\circ$C and a solution of 1 kg. of commercial $NaCN$ in 1.2 liters
II. CARBON

Fig. 212. Preparation of hydrogen cyanide. 

a) five-liter generating flask heated to 90°C; b) dropping funnel; c) condenser; d and e) filter flasks; f) ground joint flask.

of H₂O is carefully added dropwise. The decomposition ends in 1-1.5 hours. The water bath is then brought to a boil; the HCN is completely driven off within 30 minutes. Water vapor is then removed in condenser c, in filter flask d containing 20 ml. of 2N sulfuric acid and some boiling stones, and in the second filter flask e, containing 200 g. of CaCl₂ over a layer of glass wool. Both the latter and the condenser are heated to 50°C. Hydrogen cyanide is condensed in the ground joint flask f, which is cooled with ice-salt mixture. A second condensation flask is attached to the first for safety. The yield is 550 g.

II. 

$$K_4[Fe(CN)_6] + 3 H_2SO_4 = 2 K_2SO_4 + FeSO_4 + 6 HCN$$

A 200-g. portion of K₄[Fe(CN)₆] · 3H₂O, not too finely crushed, is placed in a round-bottom two-liter flask and a cold mixture of 160 g. of concentrated H₂SO₄ and 250 g. of H₂O is added. The flask is then sealed with a well-seated rubber stopper, through which a 400 mm.-long glass tube of 10 mm. I.D. is inserted. The upper end of the tube connects to a narrow tube, which in turn is connected to three CaCl₂ tubes placed in series below it. These tubes are immersed up to their necks in a 40°C water bath. The last tube has a three-way stopcock which permits discharge to the hood. This stopcock is connected to a mercury check valve, which in turn is connected to a Liebig condenser, the bottom end of which is connected to a well-cooled round-bottom flask by means of a two-hole rubber stopper. An outlet to the hood passes through the other hole.
The flask should be gently heated (sand bath or asbestos plate). The HCN condenses in the Liebig condenser and in the round-bottom flask.

Purification is accomplished by three further distillations, discarding each time the first and last fractions. The material is then fractionated in a vacuum column. High vacuum is used when maximum purity is required.

Storage of HCN: Two drops of concentrated hydrochloric acid are added to the flask, which is then stored in an ice chest. The stopper of the flask should be secured with a wire lock.

Other preparative method: From Hg(CN)₂ and H₂S [J. R. Partington and M. F. Caroll, Phil. Mag. (6) 49, 665 (1925)].

SYNONYMS:
Hydrocyanic acid, formyl nitrile, prussic acid.

PROPERTIES:

Burns with a red-blue flame. Miscible with water, alcohol and ether in all proportions. Weak acid.
d (0°C) 0.715, d (liq., 18°C) 0.691. Heat of formation 30.7 kcal./mole.

REFERENCES:

Cyanogen (CN)₂

\[
2 \text{CuSO}_4 + 4 \text{KCN} = 2 \text{CuCN} + 2 \text{K}_2\text{SO}_4 + (\text{CN})_2
\]

Potassium cyanide solution is permitted to drip on 500 g. of finely pulverized CuSO₄ · 5H₂O placed in a two-liter round-bottom flask with a two-hole stopper for a dropping funnel and gas outlet tube. The rate of addition is determined by the desired rate of gas evolution. If the rate of evolution of (CN)₂ becomes too low, the flask is heated on a water bath. The (CN)₂ passes through an empty, ice-cooled wash bottle and then a CaCl₂ tube and is condensed in a receiver held at -55°C.
To regenerate the CuCN formed in the flask, the liquid is de­canted (after the evolution of gas has ceased) and about 1.2 liters of FeCl₃ solution (d 1.26) is added to the moist cyanide, after which further (CN)₂ may be generated.

For purification, (CN)₂ is passed through an evacuated P₂O₅ tube (300 mm, long, 30 mm, I.D.) and condensed in a flask cooled with liquid nitrogen. The condensate may be redistilled in high vacuum.

II. PREPARATION BY THERMAL DECOMPOSITION OF AgCN

A) SILVER CYANIDE AgCN

\[ \text{AgNO}_3 + \text{KCN} = \text{AgCN} + \text{KNO}_3 \]

A cold, saturated solution of AgNO₃ is precipitated with the stoichiometric quantity of 78% solution of KCN; the AgCN is rapidly filtered and immediately heated with ammonia (d 0.88). The AgCN that precipitates on cooling is twice recrystallized from ammonia in the same manner and is then dried for four days at 140°C to remove NH₃ and H₂O.

Pale brown powder, stable to light, very slightly soluble in acids.

B) CYANOGEN (CN)₂

\[ 2 \text{AgCN} = (\text{CN})_2 + 2 \text{Ag} \]

Pulverized AgCN is charged into a Vycor tube connected to a high-vacuum apparatus. The substance is first outgassed in high vacuum at 280-330°C and then heated to 330-380°C, which results in its decomposition and generation of (CN)₂. The gas is passed through a P₂O₅ drying tube and condensed in a receiver cooled with liquid nitrogen. The product, already relatively pure, is refractionated in high vacuum.

Other preparative method: Thermal decomposition of Hg(CN)₂. However, the use of AgCN is more advantageous, because the Hg(CN)₂ readily sublimes without releasing (CN)₂ [J. H. Perry and D. C. Bardwell. J. Amer. Chem. Soc. 47, 2629 (1925)].

SYNONYMS:

Dicyanogen, oxalic acid dinitrile.
PROPERTIES:


Burns with a peach-blossom-colored, blue-edged flame; mixtures containing 14 vol.% $O_2$ are explosive.

Soluble in $H_2O$, alcohol and ether. The solutions quickly decompose. Polymerizes to solid, brown-black paracyanogen on heating or even in sunlight. Forms HCN and HNCO ("pseudo-halogen") with water.

$d$ (b.p.) 0.954. Heat of formation 62.0 kcal./mole.

REFERENCES:


Cyanogen Chloride

$CNCI$

$I. \quad K_2[\text{Zn(CN)}_4] + 4 \text{Cl}_2 = 4 \text{CNCI} + 2 \text{KCl} + \text{ZnCl}_2$

\[
\begin{align*}
247.6 & \quad 283.6 & \quad 245.8 & \quad 149.1 & \quad 136.3
\end{align*}
\]

A solution of 130 g. of KCN in 200 ml. of water is added to a solution of 145 g. of $\text{ZnSO}_4 \cdot 7 \text{H}_2\text{O}$ in 200 ml. of water held in flask a (see Fig. 213). This results in a suspension of $K_2[\text{Zn(CN)}_4]$ in 400 ml. of water. The suspension is vigorously stirred with a ground glass stirrer, the apparatus is purged with $N_2$, and Cl$_2$ is introduced through a fritted glass filter. At a Cl$_2$ rate of 8 to 10 bubbles per second, a steady, fast stream of CNCI is produced 1-1.5 hours after the start of the run. Prior to gas generation the mixture evolves some heat. This is removed by cooling with running water so as to keep the temperature below 20$^\circ$C. Foam is broken up by the stirrer in the broad upper section of the reaction flask. The product is dried over CaCl$_2$ and is frozen out in a receiver cooled with an ice-salt mixture or, even better, with Dry Ice-acetone. After one half of the required quantity has
II. CARBON

Fig. 213. Preparation of cyanogen chloride.

been introduced the Cl₂ stream rate is reduced every hour by 2 to 3 bubbles per second, so that no unreacted Cl₂ can contaminate the product. After five hours the reaction mixture clears up. The Cl₂ flow is interrupted and the residual CNCI is driven off with N₂.

The yield of pure CNCI is 98%, based on KCN, and 85% based on Cl₂. The product requires no further purification. It is entirely free of chlorine. The content of possible impurities other than chlorine is less than 0.1%. The cation bound to the [Zn(CN)₄]²⁻ complex is not important. Experiments with Na₂[Zn(CN)₄] and Ca[Zn(CN)₄] result in equally satisfactory yields and equally pure products.

\[
\text{NaCN} + \text{Cl}_2 = \text{NaCl} + \text{CNCI} \\
49.0 \quad 70.9 \quad 58.4 \quad 61.5
\]

Pulverized NaCN (49 g.) and 170 ml. of CCl₄ are charged into a 500-ml. three-neck flask (see Fig. 214), provided with a mercury seal stirrer and gas inlet and outlet tubes. The flask is cooled to -5 to -10°C in an ice-salt mixture, and the air is displaced with N₂. Now 2 ml. of glacial acetic acid is added to the reaction mixture, the stirrer is started, and Cl₂ is introduced. The Cl₂ flow rate is adjusted to assure its complete absorption. No gas bubbles
should form in the wash bottle attached in series with the apparatus. The temperature must be rigorously held at \(-5^\circ\text{C}\) or less, since otherwise CNC\(_1\) reacts with NaCN to form (CN)\(_2\). The reaction ends after about 4.5 hours. The chlorine flow is stopped, the receiver is cooled to \(-40^\circ\text{C}\) with Dry Ice-acetone, the spiral condenser is encased in an ice-salt mixture, and a slow N\(_2\) stream is passed through the apparatus. The temperature of the three-neck flask is allowed to rise to 60-65°C over a period of 1-1.5 hours, so that all the CNC\(_1\) distills. The Cl\(_2\) dissolved in the CNC\(_1\) can be removed either by placing a distillation column cooled with a \(-25^\circ\text{C}\) bath over the Erlenmeyer flask containing the distillate, the CNC\(_1\) being permitted to reflux while gaseous Cl\(_2\) escapes; or by freezing the product at \(-79^\circ\text{C}\), removing the Cl\(_2\) in a vacuum apparatus, and fractionating the residue. The yield is 44-47 g. (72-77%).

**PROPERTIES:**

Colorless liquid or colorless, lachrymatory gas. M.p. \(-6.5^\circ\text{C}\), b.p. 13°C; d (4°C) 1.218. Vapor pressure (0°C) 445 mm. Attacks Hg slightly. Pure CNC\(_1\) does not polymerize. Exceptionally poisonous. Therefore, all work must be done under a good hood. The experimenter is strongly advised to protect himself with a gas mask when working with CNC\(_1\). Solubility: 2.5 liters in 100 ml. of water (20°C); 10 liters in 100 ml. of alcohol (20°C); 5 liters in 100 ml. of ether (20°C).

**REFERENCES:**


**Cyanogen Bromide**

\[
\text{CNBr}
\]

\[
\text{Br}_2 + \text{NaCN} = \text{NaBr} + \text{CNBr}
\]

One kilogram of \(\text{Br}_2\) (320 ml.) is covered with 150 ml. of water in a two-liter ground joint flask placed under a good hood. The stirrer is then turned on and a solution of 420 g. of \(\text{NaCN}\) (i.e., one third excess) in 850 ml. of water is added at the rate of 1 drop per second. The temperature of the mixture must be kept below 20°C. Any local excess of cyanide is carefully avoided because it leads to formation of \((\text{CN})_x\). The last 150 ml. of the \(\text{NaCN}\) solution is diluted with twice that amount of water. Further dropwise addition of the solution is best performed manually, and the flask should be vigorously shaken by hand after each addition. When a persistent brown tint appears the rest of the \(\text{NaCN}\) solution is discarded. The addition of \(\text{NaCN}\) takes about five hours.

As shown in Fig. 215, a large diameter tube bent into a V is attached to the round-bottom flask. The shorter arm of the tube is filled with granular \(\text{CaCl}_2\). The flask is placed on a water bath and the \(\text{CNBr}\) is distilled. It is collected in a 750-ml. powder bottle serving as receiver. The yield of snow-white crystals is 590 g. or 90% of theoretical, based on \(\text{Br}\). The material can be stored in this form for a long time. Brownish \(\text{CNBr}\) is not stable.
The bottles used for storage are preferably closed with corks well coated with paraffin rather than with glass stoppers.

II. A modification of the process in terms of the quantities required is reported by Hartmann and Dreger. Half a kilogram of Br₂ is covered with 50 ml. of water and treated with a solution of 170 g. of NaCN (i.e., about 1/8 more than the stoichiometric) in 1200 ml. of water (i.e., 2.5 times as much as in method I). The yield is 73-85%.

III. Other preparative method: To avoid loss of half the Br₂ in by-product NaBr, Zmaczyński recommends the reaction:

\[ 2\text{KCN} + \frac{1}{4}\text{H}_2\text{SO}_4 + \text{Br}_2 + \text{Cl}_2 = \frac{1}{2}\text{K}_2\text{SO}_4 + \text{KCl} + \text{HCl} + 2\text{CNBr} \]

The stoichiometric quantities of H₂SO₄ and Br₂ are added to a KCN or NaCN solution. At the end of the reaction the same quantity of KCN or NaCN is added and Cl₂ is introduced until one drop of the solution causes starch-iodide paper to turn blue. The temperature must be held at 0 to +5°C during the entire process. Further treatment follows that described in method I.

PROPERTIES:

Formula weight 105.93. Colorless needles. M.p. 52°C, b.p. 61.6°C; d (20°C) 2.01. Soluble in ether. Because of the high toxicity of the product, all work must be done under an efficient hood. The experimenter should wear a gas mask.

REFERENCES:


Cyanogen Iodide

CNI

I. NaCN + I₂ = CNI + NaI

49.0 253.8 152.9 149.9

A solution of 27 g. (0.55 mole) of NaCN in 100 ml. of water is allowed to cool to 0°C in a 500-ml., ice-cooled three-neck flask provided with a stirrer and a thermometer and placed under a good hood. Then a total of 127 g. (0.5 mole) of iodine is added in portions of 3-4 g. with vigorous stirring. Each new portion is added only after the previous one has completely reacted. The CNI product
II. CARBON

is extracted 10 minutes after the end of the addition, first with 120 ml., then with 100 ml. and finally with 80 ml. of ether. The combined ether extracts are concentrated in vacuum at room temperature. This yields 90 g. of impure, light-brown product. To remove the NaI, which is soluble in the ether solution of CNI (NaI₂(CN)), the crude product is heated to 50°C with 120 ml. of water and shaken for 15 minutes at slightly reduced pressure (about 0.5 atm.). After cooling at 0°C, the colorless, crystalline CNI is separated from the yellow mother liquor by filtration, washed repeatedly with small amounts of ice water, and dried in air (under a hood). The yield is 59 g. (77% based on I).

Cyanogen iodide of highest purity is obtained by recrystallization from chloroform. The total product is dissolved in 150 ml. of boiling chloroform and slowly cooled to −10°C. After filtering, it is again washed with some ice-cold chloroform and dried in air.

II. A modification of this process, in which half of the I₂ is not wasted to form alkali iodide, has been described by Grignard and by Zmaczyński. In accordance with the equation

\[ 2\text{KCN} + \text{I}_2 + \text{Cl}_2 = 2\text{CNI} + 2\text{KCl}, \]

\( \text{Cl}_2 \) is introduced while the KCN is reacting with the \( \text{I}_2 \), or the stoichiometric quantities of \( \text{H}_2\text{SO}_4 \) and \( \text{I}_2 \) are added to a KCN (NaCN) solution, i.e., one mole of \( \text{I}_2 \) per mole of starting cyanide. At the end of the reaction, the same amount of KCN or NaCN is added and \( \text{Cl}_2 \) is introduced until one drop of the solution turns starch-iodide paper blue. The temperature is held at 0 to +5°C during the entire process. Workup is the same as described above.

PROPERTIES:

Colorless, silky crystalline needles. M.p. (in sealed tube) 146.5°C. Sublimes. Slightly soluble in cold, and readily soluble in hot water; soluble in alcohol and ether.

REFERENCES:


Cyanic Acid

\( \text{HNCO} \)

Heating of urea yields cyanuric acid, which is converted to cyanic acid by dry distillation.
A) CYANURIC ACID (CONH)₃

Urea is heated and the resulting crude product is twice recrystallized from hot water. After the first filtration, 10 ml. of concentrated hydrochloric acid is added to one liter of the solution.

Commercial cyanuric acid is purified by recrystallization in the same manner. This step must not be omitted, as otherwise the cyanuric acid will explode on distillation at −30°C, the explosion being accompanied by polymerization.

B) CYANIC ACID HNCO

A 1-m.-long, 25-mm. I.D. Vycor tube is filled with dehydrated cyanuric acid for a length of about 700 mm. in such fashion that a narrow channel remains for dry N₂, admitted at one end of the tube. The other end of the tube is connected to a 200-ml., two-neck receiver immersed in a cooling bath (Dry Ice-ether). The flow of N₂ is started and the empty section of the tube is brought to red heat with a 250-mm.-long tubular furnace. When the empty section is hot, the end of the furnace is moved toward the cyanuric-acid-filled section and the furnace is advanced as decomposition of the acid proceeds. The reaction product, condensed in the receiver, is evacuated for several hours at −80°C (using an oil pump), shaken with P₂O₅ at −20°C, and distilled into a receiver cooled to −80°C. The final purification proceeds in high vacuum.

The connection between the reaction tube and the receiver must be of large diameter to prevent plugging. The sublimate appearing in the tube itself is not heated, as it will form a great deal of hard-to-separate HCN.

Removal of HCN. Prior to the P₂O₅ treatment, the reaction product is shaken for several hours with some Ag₂O, and distilled over P₂O₅. The operation is repeated if necessary.

The yield is 80%.

Determination of the HCN content of HNCO. A thin jet of 1 ml. of HNCO is added from a precooled pipette to 40 ml. of 0°C, 1N, vigorously shaken KOH solution. The HNCO is absorbed as cyanate. The CN⁻ ion is titrated with silver nitrate solution by the Liebig method.

PROPERTIES:

Formula weight 43.03. Colorless liquid with stifling odor. B.p. 23.5°C; vapor pressure(0°C) 271.0 mm. Soluble in water (dec.). Polymerizes below 150°C to a trimer (HNCO)₃ and converts above 150°C to cyanuric acid. At 0°C, liquid cyanuric acid polymerizes within an hour to a mixture of the two substances. Dilute solutions of cyanic acid in ether, benzene or toluene are stable for weeks. d(liq., −20°C) 1.156. Heat of formation −36.5 kcal./mole.
A mixture of KNCS and KHSO₄ is ground together as finely as possible and allowed to stand for 3-4 weeks over P₂O₅. Then flask a of an apparatus such as that shown in Fig. 216 is successively charged (the order of addition should be maintained) with 250 g. of glass beads (6-7 mm. in diameter), 100 g. of KNCS alternated with beads, then a covering layer of glass beads, then the required amount of KHSO₄ mixed with glass beads. Without disturbing these layers, the glass flask is mounted in a rigid support and joined on one side of the horizontal tube p via a ground glass spray trap f. The other ground glass joint of a is closed off with a cap.

Condensation occurs in the two vessels c and d, in series, the necks of which end in male ground joints. A manifold with ground glass joints connects one neck of each of the vessels to a mercury manometer. An iron-Constantan thermocouple, sealed into a ground joint cap, is inserted into the other neck of each vessel. A side tube from vessel c connects it to three-way stopcock h₁, and vessel d is similarly connected to three-way stopcock h₂. The latter is connected to the pump via a drying tower filled with calcium hydroxide. Air may be admitted via h₂ as required.

Before starting the reaction the vessels are thoroughly dried by heating in vacuum, and then vessel c is cooled, with the vacuum on, in a liquid nitrogen bath. The stopcock leading to drying tube p is opened. Now flask a is rotated on its axis for 5 to 10 minutes, causing the salts to mix and to be ground by the glass beads. The mixing causes HNCS to be generated, cooling flask a. It is held at room temperature by a lukewarm water bath. The mixture becomes rose-colored at first [Fe(NCS)₃] and then turns white to ivory. This color should be maintained until the reaction ends. If the mass becomes yellow, it means that HNCS is decomposing, yielding HCN. In this case, stopcock h₁ must be closed and all further gaseous product is discarded. If the preparation is properly performed, the ivory color remains for 1-1.5 hours. If repeated rotation of a results in no further generation of HNCS, the spray device b is actuated, which drenches the mass with water vapor.
Fig. 216. Preparation of hydrogen thiocyanate. 

**a)** Pyrex gas generator, two liters; 
**b)** spray device with two capillary nozzles and stopcock; 
**c)** spray trap; 
**d)** drying tube, 500 mm. long, 50 mm. I.D., filled with \( \text{P}_2\text{O}_5 \), quartz wool, and short glass rods; 
**e)** fritted glass filter; 
**f)** three-way stopcock, 20 mm. I.D.; 
**g)** condenser traps, 400 mL.; 
**h)** iron-Constantan thermocouples; 
**i)** three-way stopcock; 
**j)** Hg manometer; 
**k)** analysis tubes.

and finely divided water droplets when the stopcock is opened and flask \( a \) is vigorously rotated. Inasmuch as the addition of water significantly influences the amount and purity of the HNCS, it must be held within close limits. The control of the spray is learned with some practice. As the condensation proceeds, the Dewar flask at \( c \) is moved higher and higher, until finally the entire enlarged section of flask \( c \) is cooled. If obstructions to gas flow occur in drying tube \( p \), then the tube is rotated a few times. The run is ended after 1 to 1.5 hours by closing stopcock \( h_1 \). It is terminated earlier if the mass in the flasks becomes yellow or the \( \text{P}_2\text{O}_5 \) in tube \( p \) is exhausted or becomes bright yellow at the points where an obstruction to flow is produced (decomposition of concentrated HNCS solutions in the presence of mineral acids). Finally the product is distilled (in high vacuum) from \( c \) into \( d \). The preparation is virtually pure (m.p. checked with thermocouple \( t_2 \)). The yield is 15-20 g. of solid HNCS.

**Analysis of the solid condensate.** One part of the substance is distilled into tube \( h \), constricted for sealing off (Fig. 216). This tube
is then fused and removed from the apparatus, placed in a measured quantity of excess 0.1N KOH, and the tip is broken off. Removal of the glass fragments by filtration and weighing gives the weight of material by difference A 100-ml. portion of the filtrate is diluted to 250 ml. and the excess KOH is back-titrated with 0.1N HCl. Another 100 ml. of the filtrate is acidified with nitric acid, and the HNCS content is determined by the Volhard method.

*Test for HCN.* Volhard method: Titration with AgNO₃ solution in the presence of KI [L. Birckenbach and K. Sennewald, Liebigs Ann. Chem. 512, 38 (1934)].

*Other preparative possibility:* Preparation of a dilute aqueous solution of HNCS from NH₄NCS and water in presence of the hydrogen form of an ion-exchange resin [R. Klement, Z. anorg. allg. Chem. 260, 268 (1949)].

**SYNONYMS:**

Thiocyanic acid, sulfocyanic acid.

**PROPERTIES:**

White substance with an enamel luster. M.p. -110°C. 
Polymerizes between -90 and -85°C to a white crystalline mass. Converts with careful heating in vacuum to bright-yellow, ether-soluble thiocyanuric acid [(HNCS)₃], which readily dissolves into HNCS. If either HNCS or the yellow form is heated at room temperature without evacuation, the material slowly turns dark red, both in the presence and in the absence of air. At about +3°C, a rapid exothermic reaction occurs. The entire mass foams and coalesces into a slurry.

Miscible with water in all proportions. Dilute solutions (<5%) are stable. Very strong acid.

**REFERENCE:**

L. Birckenbach and E. Buchner, Ber. dtsch. chem. Ges. 73, 1153 (1940).

**Thiocyanogen**

(ScN)₂

1. A suspension of AgNCS in CS₂ is treated with Br₂. The AgBr is split off, releasing (ScN)₂.

A) SILVER THIOCYANATE AgNCS

\[ \text{AgNO}_3 + \text{KNCS} = \text{AgNCS} + \text{KNO}_3 \]

169.9 97.2 166.0 101.1
A solution of AgNO₃ is precipitated with the stoichiometric quantity of KNCS; the precipitate is washed by decantation, filtered and dried at 70°C.

B) THIOCYANOGEN (SCN)₂

\[
2 \text{AgNCS} + \text{Br}_2 = 2 \text{AgBr} + (\text{SCN})_2
\]

A suspension of 17 g. of AgNCS in 50 ml. of CS₂ (distilled over P₂O₅) is mixed with 8 g. of Br₂. The suspension is swirled around in the flask during addition. The reaction ends after a few minutes. The resultant AgBr (plus some AgNCS) is filtered off and the solution is cooled in a specimen tube to about −70°C (Dry ice-acetone cooling bath), precipitating (SCN)₂. The thiocyanogen is separated from the CS₂ in the apparatus illustrated in Fig. 217, almost all of which is submerged in a cooling bath held at −70°C (the fritted glass filter should be about 2 cm. below the surface). When filtration is complete, the filter tube is immediately closed off with a rubber stopper and the apparatus is evacuated. After a while, dry air is introduced, the apparatus is removed from the cooling bath, and the receiver containing the mother liquor is rapidly replaced by an empty one. Some concentrated H₂SO₄ is placed in the latter to absorb moisture. The apparatus is then replaced in the cooling bath and evacuated, and once again dry air is introduced after a period of standing in the bath. The operation is repeated three or four times. The yield is 4-5 g. of (SCN)₂ (70-90%).

II. Very pure thiocyanogen is obtained by dissociation of nitrosyl thiocyanate in vacuum.

\[
\text{NOCl} + \text{KNCS} = \text{ONSCN} + \text{KCl}
\]

The starting materials are NOCl, free of chlorine and nitric oxide, 2 to 4 g. of which is sealed into ampoules with break-off ends, and anhydrous KNCS, somewhat less than stoichiometrically required for reaction with the NOCl (1 g. of NOCl is equivalent to 1.484 g. of KNCS). About 25 ml. of liquid SO₂ per g. of NOCl (the SO₂ is dried over P₂O₅) is used as the solvent. Finally, a high-vacuum apparatus must be available, to which the
dumbbell apparatus of Fig. 218 and a Stock tip breaker (Fig. 35) can be attached. The latter is used for opening the nitrosyl chloride ampoules.

The KNCS is introduced into the bottom sphere I, and enough SO₂ is condensed on it to cover the salt with a 1.5-cm. layer of liquid. The suspension is then frozen in a liquid-nitrogen bath and the NOCl and finally the remaining SO₂ are condensed on top of the frozen layer. The reaction begins immediately after thawing. The apparatus must be occasionally agitated. The reaction temperature should be about —30°C.

After one hour the resulting deep-red suspension is cooled to —50°C. The apparatus must be immersed in the cooling bath to above the level of the fritted glass filter. The product is evaporated by cooling the flask that originally contained the solvent in a liquid-nitrogen bath. The NOSCN product decomposes at the same time, liberating NO, which is also frozen by the liquid-nitrogen bath. The evaporation must be performed slowly and with care and requires about 10 hours. After the red NOSCN color has almost entirely disappeared, the same amount of solvent is again condensed on the colorless (SCN)₂ and the solution is filtered into sphere II. After another careful evaporation at —30°C, completely colorless, pure (SCN)₂ is obtained in 100% yield.

Additional preparative method: Electrolysis of NH₄NCS in methyl alcohol solution [H. Kerstein and R. Hoffmann, Ber. dtsch. chem. Ges. 57, 491 (1924)].

PROPERTIES:

White to pale yellow crystals. M.p. 15-16°C. At room temperature, explosive conversion to a brick-red, solid material. Decomposed by water to HCN, HNCS and H₂SO₄. When SCN⁻ is added to an aqueous (SCN)₂ solution, pale yellow (SCN)₅ is formed. More electronegative than I⁻; liberates I₂ from iodides. Soluble in alcohol, ether, CS₂ and CCl₄.

REFERENCES:

Ammonium Trithiocarbonate

\((\text{NH}_4)_2\text{CS}_3\)

Ammonium pentasulfide (see p. 369) is digested with \(\text{CS}_2\) in a wide-neck flask equipped with a reflux condenser and an immersed, water-cooled coil. Colorless \((\text{NH}_4)_2\text{S}\) precipitates on the cold surface of the cooling tube, but is later converted to the pale orange-yellow thiocarbonate.

Other preparative methods: A pure product is obtained from liquid \(\text{NH}_3\), \(\text{H}_2\text{S}\) and \(\text{CS}_2\).

Properties:

Formula weight 144.27. Pale orange-yellow, very hygroscopic crystals. Decomposes forming \(\text{CS}_2\) and \((\text{NH}_4)_2\text{S}\), or \(\text{CS}_2\), \(\text{NH}_3\) and \(\text{NH}_4\text{HS}\). After a long time, the thiocyanate is also formed.

Very soluble in water; slightly soluble in alcohol and ether, soluble in liquid \(\text{NH}_3\), giving a dark-red color. Red, oily \(\text{H}_2\text{CS}_3\) is produced on addition of concentrated hydrochloric or sulfuric acids.

References:


Barium Trithiocarbonate

\(\text{BaCS}_3\)

Prepared by the action of \(\text{CS}_2\) on \(\text{Ba(HS)}_2\) solution.

Barium hydroxide is dissolved in \(\text{CO}_2\)-free distilled water and any precipitated \(\text{BaCO}_3\) is filtered off in a nitrogen atmosphere. The solution is then saturated with \(\text{H}_2\text{S}\). A \(\text{CS}_2\)-saturated stream of \(\text{N}_2\) is then bubbled through the solution. After addition of ether, the red solution precipitates yellow \(\text{BaCS}_3\). It is separated from the aqueous phase and dried in vacuum or in a stream of \(\text{N}_2\).

Other preparative methods: I. Carbon dioxide-free \(\text{Ba(OH)}_2\) is suspended in alcohol, the air is displaced with \(\text{N}_2\), and a \(\text{CS}_2\)-saturated stream of \(\text{N}_2\) is bubbled through the solution. The \(\text{Ba(OH)}_2\) disappears and a yellow precipitate is produced. This is further treated as described above.

II. According to R. Klement and W. Schmidt [Naturwiss. 42, 154 (1955)] \(\text{BaCS}_3\) can also be obtained on an ion exchanger. A strongly basic \(\text{OH}^-\) form anion exchanger is converted to the \(\text{S}\) form by means
of aqueous $\text{H}_2\text{S}$ or $\text{Na}_2\text{S}$. The ion exchanger acquires a greenish color. After washing with water, $\text{CS}_2$ is added to the aqueous suspension of exchanger in an amount corresponding to the exchange capacity. The mixture is shaken until no $\text{CS}_2$ droplets can be discerned. Thus, for example 50 g. of air-dried Amberlite IRA 410 (exchange capacity 4.2 meq./g.) and 4 g. of $\text{CS}_2$ may be used. The ion exchanger, which is now salmon-colored, is placed in an ordinary glass column and eluted with 1.5N $\text{BaCl}_2$ until the yellow color of the eluate disappears. When ethanol is added to the eluate, 16 g. of analytically pure $\text{BaCS}_3$ (62% of theoretical) is obtained. The exchanger may be reused after successive treatment with acid (2N $\text{HCl}$, for example), base and sulfide.

**Properties:**

Formula weight 245.57. Yellow, microcrystalline powder or yellow, hexagonal double pyramids; stable in air; dissolves in water, giving a red color. On heating, decomposes to $\text{BaS}$ and $\text{CS}_2$.

Solubility: 1.08 g./100 g. of $\text{H}_2\text{O}$ (0°C), 1.5 g./100 g. of $\text{H}_2\text{O}$ (20°C). An aqueous solution of $\text{BaCS}_3$ dissolves one atom of S per molecule of trithiocarbonate. Heat of formation $-130.1$ kcal./mole.

**References:**


G. Gattow. Symposium über Thermodynamik in Fritzen-Watten (Symposium on Thermodynamics at Fritzen-Watten, Austria), August 20–25, 1959, 19 (1-3), 1959.