CYANIDES

1. Hydrogen Cyanide

1.1. Introduction. Hydrogen cyanide [74-90-8] (hydrocyanic acid, prussic acid, formonitrile), HCN, is a colorless, poisonous, low viscosity liquid having an odor characteristic of bitter almonds. It was prepared in dilute solution by Scheele in 1782 and as the pure compound by Gay-Lussac in 1815. The compound has been known and used as a poison for decades (see POISONS, COMMERCIAL). In England, hydrogen cyanide was sold in small crates of glass bottles for the fumigation of old furniture being rehabilitated for sale as antiques. In the United States, hydrogen cyanide was used for fumigation in the orange groves in California. It was transported to the groves by horse-drawn carts in

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milk cans. Although until the 1960s hydrogen cyanide was used as a fumigant in grain silos, this use has virtually disappeared. Hydrogen cyanide is used, however, in the manufacture of many important chemicals.

It is theorized that hydrogen cyanide played the key role in the origin of plant and animal life on earth via formation of amino acids (1,2). Hydrogen cyanide is present in the normal human being's blood. People who smoke or who consume vegetables having relatively high cyanide content have slightly higher blood concentrations.

Some hydrogen cyanide is formed whenever hydrocarbons (qv) are burned in an environment that is deficient in air. Small concentrations are also found in the stratosphere and atmosphere. It is not clear whether most of this hydrogen cyanide comes from biological sources or from high temperature, low oxygen processes such as coke production, but no accumulation has been shown (3).

In early times hydrogen cyanide was manufactured from beet sugar residues and recovered from coke oven gas. These methods were replaced by the Castner process in which coke and ammonia were combined with liquid sodium to form sodium cyanide. If hydrogen cyanide was desired, the sodium cyanide was contacted with an acid, usually sulfuric acid, to liberate hydrogen cyanide gas, which was condensed for use. This process has since been supplanted by large-scale plants, using catalytic synthesis from ammonia and hydrocarbons.

Hydrogen cyanide is a basic chemical building block for such chemical products as adiponitrile to produce nylon, methyl methacrylate to produce clear acrylic plastics (see ACRYLIC ESTER POLYMERS), sodium cyanide for recovery of gold (see GOLD AND GOLD COMPOUNDS), triazines for agricultural herbicides (qv), methionine for animal food supplement (see FEEDS AND FEED ADDITIVES), chelating agents (qv) for water treatment, and many more.

1.2. Properties. The physical properties of hydrogen cyanide are listed in Table 1.

Hydrogen cyanide is a weak acid; its ionization constant is of the same magnitude as that of the natural amino acids (qv). Its structure is that of a linear, triply bonded molecule, $HC{\equiv}N$.

Hydrogen cyanide, as the nitrile of formic acid [64-18-6], CH_2O_2, undergoes many of the typical nitrile reactions. For example, it can be hydrolyzed to formic acid by aqueous sulfuric acid (4); it can be hydrogenated to methylamine [74-89-5], CH_5N (5); and it can be converted to phenylformamidine [618-39-3], $C_7H_8N_2$, using aniline and hydrogen chloride (6).

Hydrogen cyanide can be oxidized by air at 300–650°C over silver (7) or gold (8) catalyst to give yields of up to 64% cyanic acid [420-05-3], HOCN, and 26% cyanogen [460-19-5], $(CN)_2$. Reaction with chlorine in the liquid phase gives cyanogen chloride [506-77-4], CClN (9, 10), which is the basic route to triazines of which melamine [108-78-1], $C_3H_6N_6$, is an important derivative (see CYANAMIDES; UREA). Bromine reacts similarly, but the reaction with iodine is incomplete. Chlorination in the vapor phase can be controlled to give cyanogen(11), cyanogen chloride, or cyanuric chloride [108-77-0], $C_3Cl_3N_3$ (12) (see CYANURIC AND ISOCYANURIC ACIDS).

Hydrogen cyanide adds to an olefinic double bond most readily when an adjacent activating group is present in the molecule, eg, carbonyl or cyano groups. In these cases, a Michael addition proceeds readily under basic catalysis,

Table 1. **Physical Properties of Hydrogen Cyanide**

Property	Value
molecular weight	27.03
melting point, °C	−13.24
triple point, °C	−13.32
boiling point, °C	25.70
density, g/mL	
0°C	0.7150
10°C	0.7017
20°C	0.6884
specific gravity of aqueous solutions[a]	
10.04% HCN	0.9838
20.29% HCN	0.9578
60.23% HCN	0.829
vapor pressure, kPa[b]	
−29.5°C	6.697
0°C	35.24
27.2°C	107.6
vapor specific gravity, at 31°C[c]	0.947
surface tension at 20°C, mN/m (=dyn/m)	19.68
liquid viscosity at 20.2°C, mPa · s(=cP)	0.2014
specific heat, J/mol[d]	
−33.1°C, liquid	58.36
16.9°C, liquid	70.88
27°C, gas	36.03
heat of fusion at −14°C, kJ/mol[d]	7.1×10^3
heat of formation, ΔH_f, kJ/mol[d]	
gas at 25°C	−130.5
liquid at 25°C	−105.4
heat of combustion, net, kJ/mol[d]	642
critical temperature, °C	183.5
critical density, g/mL	0.195
critical pressure, MPa[e]	5.4
dielectric constant	
0°C	158.1
20°C	114.9
dipole moment, gas, at 3–15°C, C · m[f]	7.0×10^{-30}
ionization constant, K, at 25°C	7.2×10^{-10}
conductivity, S/cm	3.3×10^{-6}
heat of vaporization, kJ/mol[d]	25.2
heat of polymerization, kJ/mol[d]	42.7
entropy, gas at 27°C, 100 kPa[b], J/(mol · °C)[d]	202.0
flash point, closed cup, °C	−17.8
explosive limits in air at 100 kPa[b] and 20°C, vol%	6–41
autoignition temperature, °C	538
index of refraction, liquid at 10°C	1.2675

[a] Measured at 18°C, compared to water at 18°C.
[b] To convert kPa to mm Hg, multiply by 7.5.
[c] Air = 1.
[d] To convert J to cal, divide by 4.184.
[e] To convert MPa to atm, divide by 0.101.
[f] To convert C · m to debye, divide by 3.336×10^{-30}.

as with acrylonitrile (qv) to yield succinonitrile [110-61-2], $C_4H_4N_2$, in high yield (13). Formation of acrylonitrile by addition across the acetylenic bond can be accomplished under catalytic conditions (see Acetylene-derived chemicals).

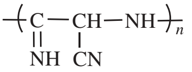
Hydrogen cyanide adds across the carbonyl group of aldehydes (qv) and ketones(qv) and opens the oxirane ring of epoxides, both under mildly basic conditions. Several of these cyanohydrins(qv) are commercially important. Acetone cyanohydrin [75-86-5] is an intermediate in the manufacture of methyl methacrylate for acrylic plastics (see Methacrylic acid and derivatives). Lactic acid [598-82-3], $C_3H_6O_3$, is made by the hydrolysis of lactonitrile [78-97-7], C_3H_5NO, which is formed from the reaction of acetaldehyde (qv) and hydrogen cyanide. Hydrogen cyanide reacts with phenols in the presence of hydrogen chloride and aluminum chloride to give aromatic aldehydes (the Gattermann synthesis). Hydrogen cyanide is a starting chemical for alanine [302-72-7], phenylalanine [63-91-2], valine [72-18-4], and aminobutyric acid.

Hydrogen cyanide reacts with formaldehyde and aniline to form *N*-phenylglycinonitrile [3009-97-0], and with formaldehyde alone to form glycolonitrile [107-16-4] (14). Hydrogen cyanide reacts with NaOH, KOH, and $Ca(OH)_2$ to form the corresponding cyanides. Amines can be derived from olefins and hydrogen cyanide via the Ritter reaction (15). Nitrilotriacetonitrile [628-87-5], $C_4H_5N_3$, is produced by the reaction of a salt of ammonia and a nonoxidizing acid with formaldehyde and hydrogen cyanide (16). Cyanogen can be formed by oxidative cleavage of hydrogen cyanide over a silver catalyst (17). Melamine can be prepared from hydrogen cyanide and NH_3 by way of cyanamide (18). Iminodiacetonitrile [628-87-5] can be prepared from hexamethylenetetramine, formaldehyde, and hydrogen cyanide (19). Oxamide [471-46-5] is formed from hydrogen cyanide and hydrogen peroxide (20). Malononitrile [109-77-3] can be produced from cyanogen chloride, acetonitrile, and hydrogen cyanide at 700°C (21). Diiminosuccinonitrile is formed from hydrogen cyanide, chlorine, and trimethylamine (22).

Cyanohydrins(qv) are formed by the reaction of glucose and similar compounds with hydrogen cyanide. The corresponding aminonitrile from methyl isobutyl ketone can be formed with ammonia and hydrogen cyanide.

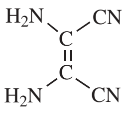
Dimethylformamide [68-12-2] can be produced from the reaction of hydrogen cyanide and methanol. Adenine [73-24-5] can be prepared from hydrogen cyanide in liquid ammonia. Thioformamide [115-08-2] can be produced from hydrogen cyanide and hydrogen sulfide.

Under certain conditions hydrogen cyanide can polymerize to black solid compounds, eg, hydrogen cyanide homopolymer [26746-21-4] (**1**) and hydrogen cyanide tetramer [27027-02-2], $C_4H_4N_4$ (**2**). There is usually an incubation period before rapid onset of polymer formation. Temperature has an inverse logarithmic effect on the incubation time. Acid stabilizers such as sulfuric and phosphoric acids prevent polymerization. The presence of water reduces the incubation period.



$$\left(\underset{\underset{\mathrm{NH}}{\|}}{\mathrm{C}}-\underset{\underset{\mathrm{CN}}{|}}{\mathrm{CH}}-\mathrm{NH}\right)_n$$

(**1**)



(**2**)

Although hydrogen cyanide is a weak acid and is normally not corrosive, it has a corrosive effect under two special conditions: (*1*) water solutions of hydrogen cyanide cause transcrystalline stress cracking of carbon steels under stress even at room temperature and in dilute solution and (*2*) water solutions of hydrogen cyanide containing sulfuric acid as a stabilizer severely corrode steel (qv) above 40°C and stainless steels above 80°C.

1.3. Manufacture and Processing. Hydrogen cyanide has been manufactured from sodium cyanide and mineral acid, and from formamide by catalytic dehydration. As of this writing, primarily because of high raw material costs, only one manufacturer uses the formamide route.

Two synthesis processes account for most of the hydrogen cyanide produced. The dominant commercial process for direct production of hydrogen cyanide is based on classic technology (23–32) involving the reaction of ammonia, methane (natural gas), and air over a platinum catalyst; it is called the Andrussow process. The second process involves the reaction of ammonia and methane and is called the Blausäure-Methan-Ammoniak (BMA) process (30,33–35); it was developed by Degussa in Germany. Hydrogen cyanide is also obtained as a by-product in the manufacture of acrylonitrile (qv) by the ammoxidation of propylene (Sohio process).

The Shawinigan process uses a unique reactor system (36,37). The heart of the process is the fluohmic furnace, a fluidized bed of carbon heated to 1350–1650°C by passing an electric current between carbon electrodes immersed in the bed. Feed gas is ammonia and a hydrocarbon, preferably propane. High yield and high concentration of hydrogen cyanide in the off gas are achieved. This process is presently practiced in Spain, Australia, and South Africa.

A process has been developed to synthesize hydrogen cyanide from coal and ammonia. This process has not yet been commercialized (38). Limited quantities of hydrogen cyanide are also recovered from coke oven gases. Hydrogen cyanide is produced when hydrogen, nitrogen, and carbon-containing compounds are brought together at high temperatures with or without a catalyst.

Examples of the variety of systems that yield hydrogen cyanide but that have not yet shown economic significance include: at 1100–1300°C acetonitrile and ammonia produce a gas containing 47.3 mol% HCN, 1.1 mol% NH_3, 0.8 mol% NO, 0.4 mol% CH_4, 0.04 mol% CH_3CN, and 49.9 mol% H_2 (39); hydrogen cyanide is produced from the reduction of nitric oxide over precious metal and perovskite catalysts at 400–800°C (40); and methanol and ammonia react in the absence of O_2 and in the presence of catalysts at 600–950°C to produce hydrogen cyanide (41).

The stoichiometry of the Andrussow process may be represented by

$$\mathrm{CH_4 + NH_3 + 1.5\ O_2 \longrightarrow HCN + 3\ H_2O}$$

$$\Delta H = +481.9\ \mathrm{kJ/mol}\ (115.2\ \mathrm{kcal/mol})$$

The oxidation of the hydrogen is not complete so that the converter off-gas contains hydrogen. The overall reaction is carried out adiabatically. This is accomplished by the addition of air (O_2). The air oxidizes a portion of the methane, making the overall reaction exothermic, even though the reaction of methane with ammonia to form hydrogen cyanide is quite endothermic.

The catalyst temperature is about 1100°C. Precious metal catalysts (90% Pt/10% Rh in gauze form) are normally used in the commercial processes. The converters are similar to the ammonia oxidation converters used in the production of nitric acid (qv) although the latter operate at somewhat lower temperatures. The feed gases to the converter are thoroughly premixed. The optimum operating mixture of feed gas is above the upper flammability limit and caution must be exercised to keep the mixture from entering the explosive range.

The reactions taking place in the Andrussow process are more complex than that shown (42). Most of the heat required for hydrogen cyanide formation is supplied by combustion of methane. The endotherm of the methane–ammonia reaction is 251 kJ/mol (60 kcal/mol) of hydrogen cyanide formed. Preventing the decomposition of ammonia and hydrogen cyanide is a critical aspect of successful operation. The equilibrium concentration of hydrogen cyanide in the converter gases at 1100°C is 0%. Therefore, to prevent hydrogen cyanide decomposition, the converter gases must be quickly quenched to $<400°C$. This is done in a steam-generating waste-heat boiler located directly below the catalyst gauze.

Modern hydrogen cyanide plants are energy cost sensitive, and recovery of heat is important. The waste-heat boiler directly below the catalyst bed accomplishes two things: (*1*) the gases are quenched to $<400°C$ to minimize hydrogen cyanide decomposition and (*2*) steam is generated to recover energy. Approximately 5 kg of steam is generated per kilogram of hydrogen cyanide. Conversion, yields, and productivity of the synthesis unit are influenced by the extent of feed gas preheat, purity of the feeds, reactor geometry, feed gas composition, contact time, catalyst composition and purity, converter gas pressure, quench time, and materials of construction.

In one patent (31), a filtered, heated mixture of air, methane, and ammonia in a volume ratio of 5:1:1 was passed over a 90% platinum–10% rhodium gauze catalyst at 200 kPa (2 atm). The unreacted ammonia was absorbed from the off-gas in a phosphate solution that was subsequently stripped and refined to 90% ammonia–10% water and recycled to the converter. The yield of hydrogen cyanide from ammonia was about 80%. On the basis of these data, the converter off-gas mol% composition can be estimated: nitrogen, 49.9%; water, 21.7%; hydrogen, 13.5%; hydrogen cyanide, 8.1%; carbon monoxide, 3.7%; carbon dioxide, 0.2%; methane, 0.6%; and ammonia, 2.3%.

There are two processes for recovering the hydrogen cyanide from the converter off-gases. One, shown in Figure 1, recovers unreacted ammonia for recycle to the converter, and the other, shown in Figure 2, scrubs the ammonia out of the gas using sulfuric acid, and produces ammonium sulfate [7783-20-2], $(NH_4)_2SO_4$, as a by-product. This ammonium sulfate can be a disposal problem, but the recycle system is rather capital and energy intensive. Ammonia must be removed from the off-gas before hydrogen cyanide can be recovered as the ammonia promotes polymerization of the hydrogen cyanide. In processes where ammonia is recovered as ammonium sulfate, it can be processed to dry crystalline ammonium sulfate.

The approach that recycles ammonia to the converter involves passing the off-gas from the converters through a solution of monoammonium phosphate at 60–80°C where the ammonia reacts to form diammonium phosphate. The

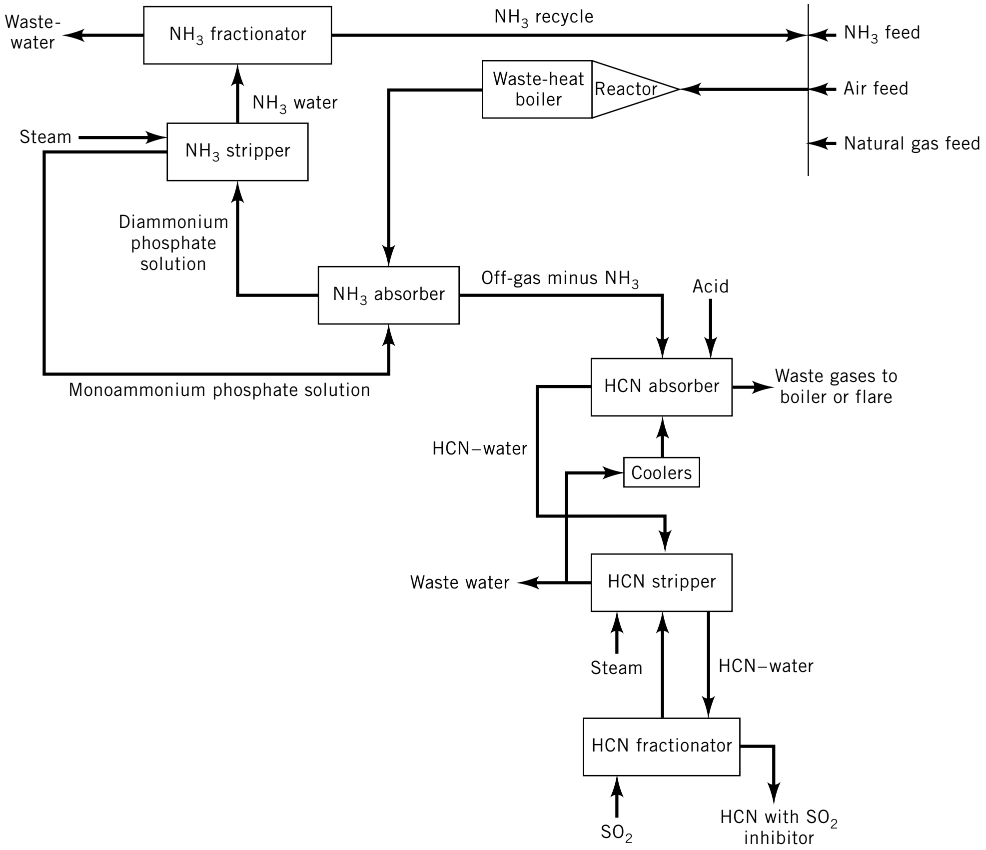


Fig. 1. Andrussow process plant with ammonia recycle.

diammonium phosphate solution is stripped back to monoammonium phosphate with steam and the ammonia–water overheads are fractionated under pressure to provide ammonia gas suitable for recycle to the converter (43). The ammonia-free off-gas from the monoammonium phosphate absorber passes to a second absorber for absorption of hydrogen cyanide in cold water. The dilute solution is stripped and fractionated by conventional means to 99.5% or higher purity. The absorber and downstream equipment are acidified with a trace of acid to avoid polymerization. A trace of sulfur dioxide is also added to the product hydrogen cyanide, which acts as stabilizer in the areas where hydrogen cyanide vapor might condense on tank or vessel ceilings. Sulfuric acid is added for supplemental stabilization. To avoid corrosion problems, all recovery equipment is constructed of austenitic stainless steel. Trace quantities of the following impurities are present in the product: cyanogen, acrylonitrile, acetonitrile, and propionitrile.

The waste gas remaining after removal of ammonia and recovery of hydrogen cyanide contains enough hydrogen and carbon monoxide that it is flammable and has enough heat value to make it a valuable fuel. It is usually used to displace other fuel in boilers.

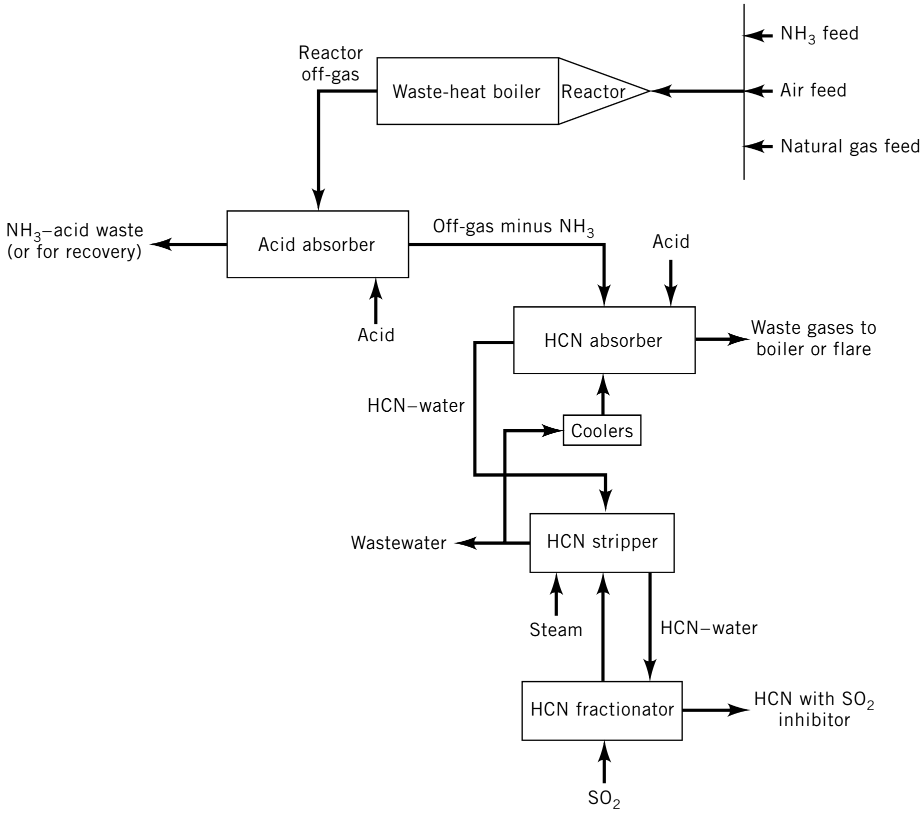


Fig. 2. Andrussow process without ammonia recycle.

Air pollution from this process is a minimal problem because all waste gases are burned for fuel value or flared. The products of combustion of the waste gases are primarily water from the hydrogen and some carbon dioxide from the carbon monoxide. Aqueous discharge is essentially the converter water of reaction, which is contaminated by traces of hydrogen cyanide and other nitriles and the ammonium sulfate. The most common treatment for this aqueous stream is alkaline chlorination, which converts cyanide to the essentially nontoxic cyanate.

The Andrussow process is by far the dominant hydrogen cyanide manufacturing process in use, even though the converter off-gas stream is dilute in hydrogen cyanide. This forces the absorbers to be large so that they can handle the large volumes of gas. Preheating Andrussow feed gases is claimed to result in an increased hydrogen cyanide concentration by supplying part of the required reaction heat without *in situ* combustion (32). Advantages of the Andrussow process are low converter investment, low maintenance costs, and high natural gas yields when the waste gas is used as fuel.

In the BMA process, methane (natural gas) and ammonia are reacted without air being present (44). The reaction is carried out in tubes that are heated externally to supply the endothermic heat of reaction very similar to a reformer. Yield from ammonia and methane is above 90%. The off-gas from the converter contains more than 20 mol% hydrogen cyanide, about 70 mol% hydrogen, 3 mol% ammonia, 1 mol% methane, and about 1 mol% nitrogen from ammonia decomposition.

A typical converter is made up of multiple furnaces, each of which contains 8 to 10 reactors. Each reactor is made up of 10 to 30 sintered alumina tubes lined with platinum. The furnaces are direct fired with natural gas to 1200–1300°C. A typical furnace can produce about 125 t per month of hydrogen cyanide. Catalyst life is approximately 10,000 h.

After removal of the unreacted ammonia and recovery of hydrogen cyanide, the waste gas is essentially all hydrogen suitable for other chemical use. The advantages of the BMA process are the high ammonia and natural gas yields and the useful hydrogen waste gas, but the high investment and maintenance for the converter is a decided disadvantage.

A significant source of hydrogen cyanide (about 30% worldwide) is as by-product from the Sohio process acrylonitrile plants. Approximately 15 kg of HCN is produced per 100 kg acrylonitrile (qv). Catalysts have been developed that improve efficiency by decreasing the amount of hydrogen cyanide produced per kilogram of acrylonitrile. This, along with the declining demand for acrylonitrile, has resulted in an ever increasing need for on-purpose hydrogen cyanide.

The fluohmic process is a third process for manufacturing hydrogen cyanide, which is being applied in Spain and Australia. This process involves the reaction of ammonia with a hydrocarbon, usually propane or butane, in a fluidized bed of coke particles. The endothermic heat of reaction is supplied electrically through electrodes immersed in the fluid bed. Yields from propane and ammonia are reportedly above 85% and the waste gas is essentially hydrogen, but the costs for electricity are high. Thus this process is applicable only when there is an inexpensive source of power.

Recovery of hydrogen cyanide from coke-oven gases has been dormant in the early 1990s, but new methods involving environmental control of off-gas pollutants may be leading the way for a modest return to the recovery of cyanide from coke-oven gases (see COAL CONVERSION PROCESS, CARBONIZATION).

1.4. Economic Aspects. Annual U.S. hydrogen cyanide capacity in 1991 was 734,000 t as shown in Table 2. U.S. production for 1983–1989 has been estimated as shown in Table 3. Output of hydrogen cyanide in the United States rose to 600,000 t/yr in 1992. Worldwide annual production and capacity of hydrogen cyanide in 1992 were estimated to be 950,000 and 1,320,000 t, respectively.

1.5. Specifications and Analysis. Hydrogen cyanide is classified by the U.S. Department of Transportation as a Class A Flammable Poison and is subject to rigid packaging, labeling, and shipping regulations. Hydrogen cyanide can be purchased in cylinders with capacities ranging from 300 mL up to 75 kg. Purchases may be made in tank car sizes of 24 and 46 t at $1.30/kg. Although there have been no accidents since the inception of bulk transportation (since 1950), the continuing trend toward reducing risk from hazardous chemicals threatens the transportation of hydrogen cyanide.

Specifications are 99.5 wt% hydrogen cyanide (min), 0.5 wt% water (max), 0.06–0.10% acidity, and color not darker than APHA 20. A combination of H_2SO_4

Table 2. **U.S. Producers of Hydrogen Cyanide and Capacities**

Producer	Capacity, 10^3 t/yr
American Cyanamid, Fortier, La.[a]	18.0
BP Chemicals[a]	50.0
Ciba Geigy Corp.	41.0
Degussa Corp.	24.0
DOW Chemical U.S.A.	9.0
E. I. du Pont de Nemours & Co., Inc.	410.0
Monsanto Co.[a]	30.0
Rohm and Haas Co.	90.0
Sterling Chemical[a]	40.0
Cyanco Co.	7.0
FMC Corp.	15.0
Total	*734.0*

[a] HCN is a by-product.

(or H_3PO_4) and SO_2 acts as a stabilizer to prevent polymerization; H_2SO_4 stabilizes the liquid phase and SO_2 stabilizes the vapor phase.

Assay of hydrogen cyanide can be done by specific gravity or silver nitrate titration. Sulfur dioxide in hydrogen cyanide can be determined by infrared analysis or by reaction of excess standard iodine solution and titration, using standard sodium thiosulfate or by measurement of total acidity by evaporation to dryness and remeasurement of acidity. Total acidity, which includes SO_2 plus H_2SO_4 or H_3PO_4, can be obtained by titration using 0.1 *N* NaOH using methyl red–methylene blue mixed indicator. Water can be determined by Karl Fischer titration.

1.6. Health and Safety Factors. The cyanides are true noncumulative protoplasmic poisons, ie, they can be detoxified readily. Cyanide combines with those enzymes at the blood tissue interfaces that regulate oxygen transfer to the cellular tissues. Unless the cyanide is removed, death results through insufficient oxygen in the cells. The warning signs of cyanide poisoning include dizziness, numbness, headache, rapid pulse, nausea, reddened skin, and bloodshot eyes. More prolonged exposure can cause vomiting and labored breathing followed by unconsciousness; cessation of breathing; rapid, weak heart beat; and death. Severe exposure by inhalation can cause immediate unconsciousness; this rapid knockdown power without an irritating odor makes hydrogen cyanide

Table 3. **U.S. Production of Hydrogen Cyanide for 1983 to 1989**

Year	Production, 10^3 t/yr
1983	330
1984	365
1985	365
1986	430
1987	470
1988	500
1989	490

more dangerous than materials of comparable toxicity, eg, H_2S. Hydrogen cyanide can enter the body by inhalation, oral ingestion, or skin absorption.

Inhalation. The threshold limit value of HCN is 4.7 ppm. This is defined as the maximum average safe exposure limit for a 15-min period by the Occupational Safety and Health Administration. Exposure to 20 ppm of HCN in air causes slight warning symptoms after several hours; 50 ppm causes disturbances within an hour; 100 ppm is dangerous for exposures of 30 to 60 min; and 300 ppm can be rapidly fatal unless prompt, effective first aid is administered. There is always a small concentration of cyanide (0.02 to 0.04 mg/L) in the blood, and the body has a mechanism for continuous removal of small amounts, such as from smoking, by converting it to thiocyanate, which is discharged in the urine.

Skin Absorption. Normal skin absorbs HCN slowly. However, 2% HCN in air may cause poisoning in 3 min, 1% is dangerous in 10 min, and 0.05% may produce symptoms after 30 min, even though a gas mask or air mask is worn. Some areas of the body, such as the feet and mucous membranes, are more absorptive than others. Cuts and abrasions absorb cyanide rapidly, and 50 mg of HCN absorbed through the skin can be fatal.

Ingestion. Ingestion, unless prompt first aid or medical treatment is given, is rapidly fatal; 1 mg of cyanide per kilogram of body weight can be fatal. Immediate and repeated administration of emetics and regurgitation (if the victim is conscious), followed or accompanied by the first aid and medical treatments described below should be carried out. If the victim is unconscious, stomach lavage should be performed by a physician or trained personnel.

First Aid and Medical Treatment. Before using or handling cyanides, intensive training in the proper first-aid protocol is essential. In case of an accident, action should be fast and efficient. With the protection of a gas mask remove or drag the victim to fresh air. Remove contaminated clothing and rinse contaminated body areas. Keep victim warm. If the victim is conscious and speaking, no treatment is necessary. If the victim is unconscious but breathing, break an ampul of amyl nitrite in a cloth and hold it under the victim's nose for 15 s. Repeat five or six times. Use a fresh ampul every 3 min. Continue until the victim regains consciousness. Amyl nitrite is a powerful cardiac stimulant and should not be used more than necessary. If the patient is not breathing, apply artificial respiration; this can best be done using an oxygen resuscitator. The amyl nitrite antidote should also be administered during resuscitation. Mouth-to-mouth resuscitation is the next-best method followed by the Holger-Mielsen arm-lift method.

Notify a physician immediately. A suggested procedure for physicians or nurses is intravenous administration of 0.3 g (10 mL of a 3% solution) of sodium nitrite at the rate of 2.5 mL/min followed by 12.5 g (50 mL of a 25% solution) of sodium thiosulfate at the same rate. Watch the patient for 24 to 48 h, especially in cases of ingestion or skin absorption. If symptoms reappear, repeat the injections in half the original amounts. These solutions should be kept readily available. In some cases, first aid personnel have been trained to use the intravenous medication subject to government regulations.

Detection. Many people can detect hydrogen cyanide by odor or taste sensation at the 1 ppm concentration in air, most at 5 ppm, but HCN does not have an offensive odor and a few people cannot smell it even at toxic levels. Anyone planning to work with hydrogen cyanide should be checked with a sniff test employing a known safe concentration. This test should be given periodically. Several chemical detection and warning methods can be employed. The most reliable are modern, electronic monitors based on electrolytes that react with hydrogen cyanide.

Disposal. Small quantities of concentrated hydrogen cyanide can be burned in a hood in an open vessel. Large-scale burning in outdoor pans can be performed, but special safety precautions must be employed. A cyanide solution can be decontaminated by making the solution strongly basic (pH 12) with caustic and pouring it into ferrous sulfate solution. The resulting ferrocyanide is relatively nontoxic. Cyanide solution can be converted to less toxic cyanate by treatment with chlorine, sodium or calcium hypochlorite, or ozone at pH 9 to 11. A solution of 10% hypochlorite maximum should be used. The final solution should be checked for absence of free cyanide. The hypochlorite or $Cl_2 + NaOH$ method is by far the most widely used commercially (45). However, other methods are oxidation to cyanate using hydrogen peroxide, ozone, permanganate, or chlorite; electrolysis to CO_2, NH_3, and cyanate; hydrolysis at elevated temperatures to NH_3 and salts of formic acid; air or steam stripping at low pH; biological decomposition to CO_2 and N_2; chromium treatment to give oxamides; nitrite or nitrate treatment to give carbonates and nitrogen; removal by ion exchange and recovery; lime–sulfur reaction to give sulfate, carbonate, and free sulfur; and gamma-ray treatment to give nontoxic constituents.

Environmental. The toxicity of cyanide in the aquatic environment or natural waters is a result of free cyanide, ie, as HCN and CN^-. These forms, rather than complexed forms such as iron cyanides, determine the lethal toxicity to fish. Complexed cyanides may revert to free cyanide under uv radiation, but the rate is too slow to be a significant toxicity factor. Much work has been done to establish stream and effluent limits for cyanide to avoid harmful effects on aquatic life. Fish are extremely sensitive to cyanide, and the many tests indicate that a free cyanide stream concentration of 0.05 mg/L is acceptable (46), but some species are sensitive to even lower concentrations.

Another important environmental issue is the fate of cyanide. Hydrogen cyanide, if spilled, evaporates quite readily. That which does not evaporate is soon decomposed or rendered nonhazardous by complexing with iron in the soil, biological oxidation, or polymerization.

General Safety Aspects. Whereas cyanides have become infamous as poisons in part because of the use in prison execution chambers, Nazi death camps, and in over-the-counter drug tampering cases, there is worldwide safe production of nearly one million t annually.

Laboratory work with hydrogen cyanide should be carried out only in a well-ventilated fume hood. Special safety equipment such as air masks, face masks, plastic aprons, and rubber gloves should be used. A chemical proof suit should be available for emergency. Where hydrogen cyanide is handled inside a building, suitable ventilation must be provided. The people involved should be thoroughly trained in first aid.

The most important rule when working with hydrogen cyanide is never to work alone. This applies especially to sampling and opening lines and equipment. A second person must be in view at all times about 9 to 10 m away, must be equipped to make a rescue, and must be trained in first aid for hydrogen cyanide exposure.

Besides toxicity, hydrogen cyanide presents other hazards. Hydrogen cyanide undergoes an exothermic polymerization at conditions of pH 5 to 11. This polymerization can become explosively violent, especially if confined. The reaction is between hydrogen cyanide and cyanide ions, so the presence of water and heat contribute to the onset of this polymerization. Stored hydrogen cyanide should contain less than 1 wt% water, should be kept cool, and should be inhibited with sulfuric, phosphoric, or acetic acid. Manufacturers recommend a maximum of 90-day storage even for inhibited hydrogen cyanide. Cylinders should not be used as heated vaporizers as the elevated temperature accelerates the reaction of the stabilizing acid with the cylinder walls which can lead to an explosive polymerization. The presence of any contaminant or surface that depletes the acid stabilizer can cause polymerization, which is first indicated by a yellow-brown color in the hydrogen cyanide followed by development of heat. Prompt action to be taken includes reacidification and cooling. The resulting polymer is nontoxic except, of course, for any hydrogen cyanide that may be occluded in the polymer.

Explosively violent hydrolysis can occur if an excess of a strong acid (H_2SO_4, HNO_3, or HCl) is added to hydrogen cyanide. The reaction is fastest at or near stoichiometric ratios, eg, 1 to 2 moles H_2SO_4 per mole HCN, and can cause severe equipment damage if confined.

From a practical use standpoint there are some unique properties of hydrogen cyanide that have safety implications: (*1*) small concentrated liquid leaks form milk white icicles resulting from evaporative freezing, even in summer; (*2*) hydrogen cyanide has an unusually steep density change with temperature, eg, more than 10 times the change per degree as water; (*3*) CO_2 is soluble in hydrogen cyanide, which can cause hydrogen cyanide exposed to CO_2 during processing to foam and spout when warmed; and (*4*) this violent action also occurs when liquid hydrogen cyanide is depressurized from the superheated state. Because of its low boiling point, hydrogen cyanide can be a fire and explosion hazard.

1.7. Uses.

Estimates of various uses for hydrogen cyanide in the United States are adiponitrile for nylon, 41%; acetone cyanohydrin for acrylic plastics, 28%; sodium cyanide for gold recovery, 13%; cyanuric chloride for pesticides and other agricultural products, 9%; chelating agents such as EDTA, 4%; and methionine [63-68-3] for animal feed, 2%.

There has been a sizable shift in distribution of uses since the early 1980s. The use of hydrogen cyanide for manufacturing nylon via the adiponitrile route has expanded substantially and the use for producing sodium cyanide has also grown. Other uses have shown a more normal growth rate. Modest quantities of hydrogen cyanide go into a large number of relatively small uses, including manufacture of ferrocyanides (see IRON COMPOUNDS), acrylates, lactic acid, pharmaceuticals (qv), and specialty chemicals.

2. Sodium Cyanide

2.1. Introduction.

Sodium cyanide [143-33-9], NaCN, is a white cubic crystalline solid commonly called white cyanide. It was first prepared in 1834 by heating Prussian blue, a mixture of cyanogen compounds of iron, and sodium carbonate and extracting sodium cyanide from the cooled mixture using alcohol. Sodium cyanide remained a laboratory curiosity until 1887, when a process was patented for the extraction of gold and silver from ores by means of a dilute solution of cyanide (see METALLURGY, EXTRACTIVE). A mixture of sodium and potassium cyanides, produced by Erlenmeyer's improvement of the Rodgers process, was marketed in 1890.

The Beilby process started in 1891 and by 1899 accounted for half of the total European production of cyanide. In this process, a fused mixture of sodium and potassium carbonates reacts with ammonia in the presence of carbon. In 1900, the Castner process, in which molten sodium, ammonia, and charcoal react to give a high (98%) grade sodium cyanide, superseded the Beilby process. Sodium cyanide became an article of commerce and soon replaced potassium cyanide in all except special uses.

The Castner process has been replaced by the neutralization or wet process in which liquid hydrogen cyanide and sodium hydroxide solution react and water is evaporated. The resulting crystals are briquetted or made into granular form. During the 1950s, essentially all sodium cyanide was used in electroplating (qv) and case hardening (see METAL SURFACE TREATMENTS). Upon the removal of control of the price of gold the use of cyanides for gold recovery expanded rapidly. Western gold production grew to 950 t in 1980 and continued to grow to 1470 t in 1991 (47). As of this writing, case hardening is a minor use. The principal applications of sodium cyanide are gold and silver extraction, electroplating, synthesis of iron blues, and synthesis of a large number of chemicals.

2.2. Properties. *Physical Properties.* The physical properties of sodium cyanide are listed in Table 4. The solid phase in contact with a saturated aqueous solution at temperatures above 34.7°C is the anhydrous salt; below 34.7°C, the solid phase is sodium cyanide dihydrate [25178-25-0], $NaCH \cdot 2H_2O$. The solubility of the dihydrate in grams of sodium cyanide per 100 grams of saturated solution is 26.01, at −15°C; 32.8, at 10°C; 34.2, at 15°C; and 45, at 34.7°C. The solubility of the anhydrous salt is less dependent on temperature.

Sodium cyanide is soluble in liquid ammonia. At temperatures below −31°C, sodium cyanide pentaammoniate [69331-34-6], $NaCN \cdot 5NH_3$, separates in large flat crystals. At 15°C, 100 g anhydrous methanol dissolves 6.44 g anhydrous sodium cyanide; at 67.4°C, it dissolves 4.10 g. Sodium cyanide hemihydrate [69331-35-7], $NaCN \cdot 0.5\,H_2O$, has been obtained by recrystallization from cold 85% alcohol. The system $NaCN{-}NaOH{-}H_2O$ has been studied (48,49). Sodium cyanide is slightly soluble in formamide, ethanol, methanol, SO_2, furfural, and dimethylformamide.

Sodium chloride and sodium cyanide are isomorphous and form an uninterrupted series of mixed crystals. The ferrocyanide ion has a marked effect on the habit of sodium cyanide crystallized from aqueous solution (50). Sodium cyanide and sodium carbonate form a molten eutectic at approximately 53 wt% sodium carbonate and 465°C. The specific conductivity of molten 98% sodium cyanide is 1.17 S/cm (51).

Chemical Properties. When heated in a dry CO_2 atmosphere, sodium cyanide fuses without much decomposition. A brown-black color appears when water vapor and CO_2 are present at temperatures of 100°C below the fusion

Table 4. **Physical Properties of Sodium Cyanide**

Property	Value
molecular weight	49.015
melting point, °C	562
boiling point, °C	1530
density of solids, g/mL	
cubic	1.60
orthorhombic	1.62–1.624
molten, at 700°C	~1.22
density of solutions, at 25°C, g/mL	
10% NaCN	1.047
20% NaCN	1.098
30% NaCN	1.150
vapor pressure, kPa[a]	
800°C	0.1013
1360°C	41.8
heat capacity[b], 25–72°C, J/(g · K)[c]	1.40
heat of fusion, J/g[c]	179
heat of formation, ΔH_f°, NaCN(c), J/mol[c]	-89.9×10^3
heat of vaporization, ΔH_{vap}, J/g[c]	3041
heat of solution,[d] ΔH_{soln}, J/mol[c]	−1548
hydrolysis constant, K_h, 25°C	2.51×10^{-5}

[a] To convert kPa to mm Hg, multiply by 7.5.
[b] The heat capacity of sodium cyanide has been measured between 100 and 345 K (48).
[c] To convert J to cal, divide by 4.184.
[d] In 200 mol H_2O.

point. This color is presumably from the hydrogen cyanide polymer. Thermal dissociation of sodium cyanide has been studied in an atmosphere of helium at 600 to 1050°C and in an atmosphere of nitrogen at 1050 to 1255°C. It has been shown that the vapor phase over melt contains decomposition products (52).

In the presence of a trace of iron or nickel oxide, rapid oxidation occurs when cyanide is heated in air, first to cyanate and then to carbonate:

$$2\ \mathrm{NaCN} + \mathrm{O_2} \longrightarrow 2\ \mathrm{NaCNO}$$
$$2\ \mathrm{NaCNO} + 1.5\ \mathrm{O_2} \longrightarrow \mathrm{Na_2CO_3} + \mathrm{N_2} + \mathrm{CO_2}$$

Case hardening of steels using a sodium cyanide molten bath depends on these reactions where the active carbon and nitrogen are absorbed into the steel surface; hence the names carburizing and nitriding (see STEEL). The ease with which it is oxidized makes sodium cyanide a good reducing agent and the oxides of several metals, such as lead, tin, manganese, or copper, are readily reduced.

No reaction takes place below 500°C when sodium cyanide and sodium hydroxide are heated in the absence of water and oxygen. Above 500°C, sodium carbonate, sodium cyanamide [19981-17-0], sodium oxide, and hydrogen are produced. In the presence of small amounts of water at 500°C decomposition occurs with the formation of ammonia and sodium formate, and the latter is converted into sodium carbonate and hydrogen by the caustic soda. In the presence of excess oxygen, sodium carbonate, nitrogen, and water are produced (53).

Molten sodium cyanide reacts with strong oxidizing agents such as nitrates and chlorates with explosive violence. In aqueous solution, sodium cyanide is oxidized to sodium cyanate [917-61-3] by oxidizing agents such as potassium permanganate or hypochlorous acid. The reaction with chlorine in alkaline solution is the basis for the treatment of industrial cyanide waste liquors (45):

$$\mathrm{NaCN + 2\ NaOH + Cl_2 \longrightarrow NaCNO + 2\ NaCl + H_2O}$$

$$\mathrm{2\ NaCNO + 4\ NaOH + 3\ Cl_2 \longrightarrow 6\ NaCl + N_2 + 2\ H_2O + 2\ CO_2}$$

The pH value is usually maintained above 9 to avoid formation of nitrogen trichloride. At lower pH values, aqueous solutions react with chlorine to form cyanogen chloride (52).

Sodium cyanide, when fused with sulfur or a polysulfide, is converted into sodium thiocyanate [574-32-7]; this compound is also formed when a solution of sodium cyanide is boiled with sulfur or a polysulfide:

$$\mathrm{NaCN + S \longrightarrow NaCNS}$$

$$\mathrm{4\ NaCN + Na_2S_5 \longrightarrow 4\ NaCNS + Na_2S}$$

A solution of sodium cyanide shaken with freshly precipitated ferrous hydroxide is converted to a ferrocyanide:

$$\mathrm{6\ NaCN + Fe(OH)_2 \longrightarrow 2\ NaOH + Na_4Fe(CN)_6}$$

If the solution is acidified and a little ferric sulfate added, ferric ferrocyanide [14038-43-8], $\mathrm{Fe_4[Fe(CN)_6]_3}$, is produced. This salt has a characteristic deep blue color, and the reaction may be used to test for the cyanide.

Aqueous solutions of sodium cyanide are slightly hydrolyzed at room temperature (54) according to the reversible reaction;

$$\mathrm{NaCN + H_2O \rightleftharpoons NaOH + HCN}$$

At temperatures above 50°C, irreversible hydrolysis to formate and ammonia becomes important. If the heat of reaction is not removed, the increased temperature accelerates the decomposition and can create high pressure in a closed vessel.

$$\mathrm{NaCN + 2\ H_2O \longrightarrow NH_3 + HCOONa}$$

Hydrogen cyanide is a weak acid and can readily be displaced from a solution of sodium cyanide by weak mineral acids or by reaction with carbon dioxide, eg, from the atmosphere; however, the latter takes places at a slow rate.

In the presence of oxygen, aqueous sodium cyanide dissolves most metals in the finely divided state, with the exception of lead and platinum. This is the basis of the MacArthur process for the extraction of gold and silver from their ores that, in the case of gold, may be represented as follows:

$$4\ \mathrm{NaCN} + 2\ \mathrm{Au} + 0.5\ \mathrm{O_2} + \mathrm{H_2O} \longrightarrow 2\ \mathrm{NaAu(CN)_2} + 2\ \mathrm{NaOH}$$

The gold is then recovered from solution by precipitation with zinc dust, electrodeposit, or absorption on carbon. Sodium cyanide is used extensively in organic syntheses, especially in the preparation of nitriles (qv).

2.3. Manufacture.

Alkali cyanides became commercially significant when the electroplating process for gold and silver was discovered about 1840. In 1899, the MacArthur-Forrest cyanide process, used for the extraction of gold and silver from low grade ores, was tested successfully on a commercial scale in New Zealand and South Africa. The MacArthur process was rapidly adopted in gold fields and resulted in a phenomenal growth in the cyanide manufacturing industry. World production of alkali cyanide rose from 5900 t/yr in 1899 to 21,000 t/yr by 1915. In the early 1990s the total world capacity was estimated to be in excess of 450,000 t. Annual usage in 1989 was about 340,000 t.

The historic Castner process that was developed in the 1800s and operated throughout the world until the late 1960s is now obsolete.

$$2\ \mathrm{Na} + 2\ \mathrm{NH_3} + 2\ \mathrm{C} \longrightarrow 2\ \mathrm{NaCN} + 3\ \mathrm{H_2}$$

Lower yields and higher costs were the reasons for the obsolescence of this process.

Almost all sodium cyanide is manufactured by the neutralization or wet processes in which hydrogen cyanide reacts with sodium hydroxide solution.

$$\mathrm{HCN} + \mathrm{NaOH} \longrightarrow \mathrm{NaCN} + \mathrm{H_2O}$$

Most plants use essentially purified anhydrous liquid hydrogen cyanide (sometimes vapors) to react with NaOH, generally fed as a 50% solution to the reactor. These raw materials must be sufficiently pure to yield a high quality, 99% sodium cyanide. Sodium hydroxide having low iron content is necessary to avoid interference with crystallization in the subsequent process steps. Purified hydrogen cyanide from the Andrussow or by-product hydrogen cyanide from acrylonitrile (qv) processes are used in most commercial sodium cyanide processes. Direct absorption of hydrogen cyanide in the product gases from Andrussow reactors into NaOH solution is practiced to some extent; however, the assay of the dry product is lower (96–97%) in this case owing to higher concentrations of sodium carbonate and sodium formate.

Most modern high tonnage plants use the reaction of high purity hydrogen cyanide and aqueous sodium hydroxide in a unit system that embodies evaporation of water and crystallization of the NaCN (55). Control of the system is critical to avoid hydrogen cyanide polymer formation, which would produce an off-white product; to minimize sodium formate formation, which would reduce the product purity; and to maximize the average crystal size. Figure 3 shows a typical sodium cyanide plant flow diagram.

A German process produces a high (99%) sodium cyanide assay by absorbing the gases from a BMA-type hydrogen cyanide reactor directly in sodium

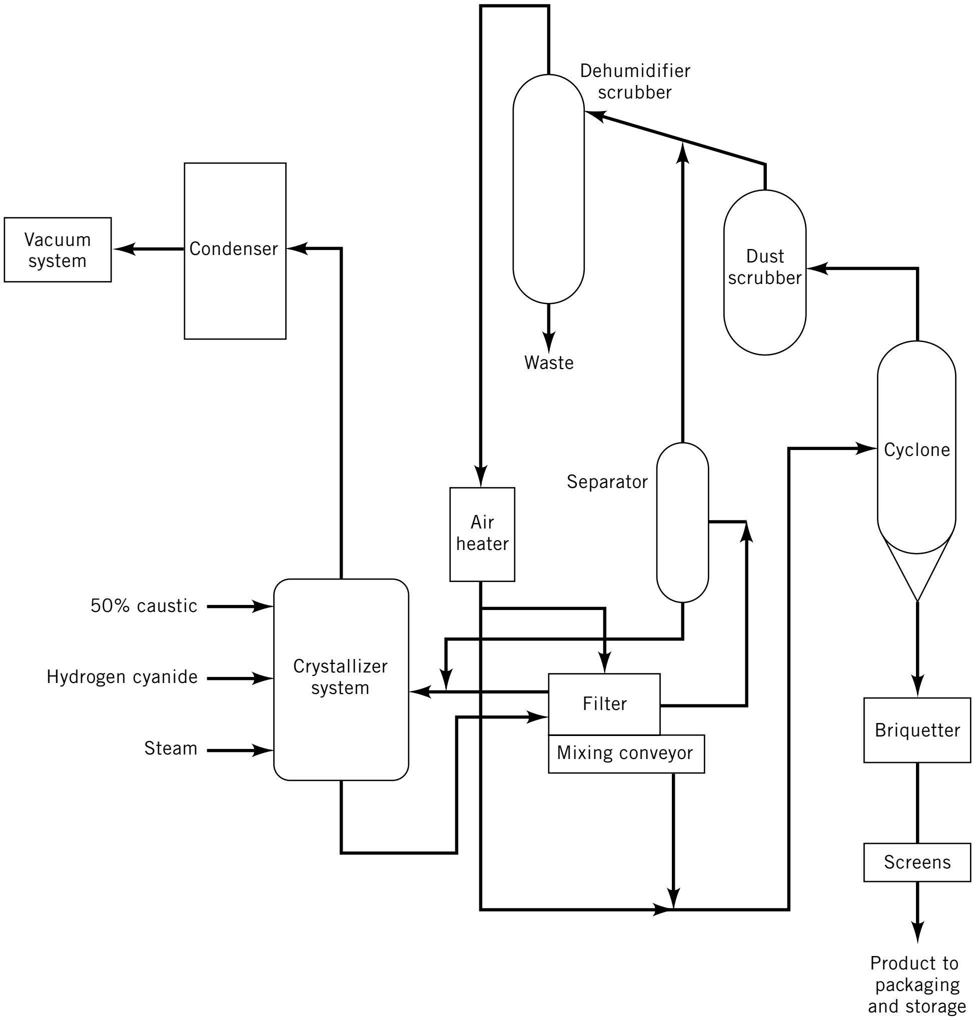


Fig. 3. Flow sheet for a sodium cyanide process.

hydroxide solution (56). The resulting sodium cyanide solution is heated in a crystallizer to remove water, and form sodium cyanide crystals.

The formation of larger crystals facilitates dewatering in the filtration step. In most modern processes, the moist salt from the filter is passed through a mixing conveyor to break up lumps. In some processes, air heated to 450°C is passed through the cake on the filter and through the mixing conveyor (57). Drying is completed in a hot-air conveyor-dryer (see DRYING). This type of adiabatic hot-air drying avoids overheating sodium cyanide when moisture is present, thereby minimizing the formation of sodium formate in the dried product. Inherently, sodium cyanide is a small (50 μm dia) crystal, that gives a dusty solid of low bulk density that must be compacted or fused into larger particles for safer handling. Melting the dry, dusty material and casting it into molds is rarely done because of the high energy requirement. Most modern processes employ mechanical compacting devices that produce either briquettes, granular products, or both (58). Briquettes or tablets are formed in approximate 15-g and 30-g sizes. The granular size is about 4 mm.

In a typical process the finely divided dry crystals are compacted under heat and pressure in a roll press into briquettes having a density of 1.550 to 1.590. The briquettes are passed to a rotary screen where the fins, thin layers of material attached to the periphery of the briquette centerline, are removed and reprocessed. The finished briquettes pass into large storage bins from where they are loaded into rail-hopper cars or shipping bins or packaged into drums and other shipping containers.

Plants for the production of sodium cyanide from Andrussow process or from acrylonitrile synthesis by-product hydrogen cyanide are operating in the United States, Italy, Japan, the UK, and Australia. In Germany, sodium cyanide is produced from BMA hydrogen cyanide, and in Australia one plant uses Fluohmic process hydrogen cyanide.

The neutralization process is not energy intensive; added heat evaporates water formed in the reaction and water entering the system with the raw materials, which is 50% NaOH. The significant waste effluent contains 10–100 ppm NaCN and must be treated before disposal.

A slight excess of NaOH must be maintained at all stages of processing to keep pH high and prevent forming color from black or brown polymer. The product as shipped must also contain a slight excess of NaOH so that clear, colorless sodium cyanide solutions result. Most sodium cyanide is sold in dry form to minimize the higher freight costs associated with shipping water. Appreciable tonnage is also sold as 30% aqueous solution.

2.4. Economic Aspects. Sodium cyanide is sold as granular or powder, pillow-shaped briquettes of 15-g and 30-g sizes, tablets of 30 g, and 30% aqueous solution. List price in 1991 was $1.85/kg.

Typical analysis for the neutralization wet process product is given in Table 5. Sodium cyanide is packed in mild steel or fiber drums and in 1.4 t Flo-bins. Dry sodium cyanide is also shipped in wet-flo tank cars and trucks of up to 32 t net. At destination, water is circulated through the wet-flo car or trailer to dissolve the dry sodium cyanide at delivery. This type of shipment reduces freight costs and reduces environmental risks compared with 30% aqueous solution shipment. Safety regulations are imposed by the various shipping lines and by the countries in which cyanide is transported.

Table 5. **Typical Analysis of Sodium Cyanide**

Constituent	Concentration
NaCN, %	98–99
Na_2CO_3, %	0.3–0.9
HCOONa, %	0.4
NaOH, %	0.3
NaCl, %	0.01
S, ppm	<1.0
H_2O, %	0.06
Fe, ppm	10–20

2.5. Analytical Methods. The cyanide content of a sodium cyanide sample may be determined by titration of an aqueous solution containing 10 g/L with 0.1 *N* silver nitrate solution. Potassium iodide is the indicator. Use of the indicator *p*-dimethylaminobenzal–rhodamine [536-17-4], $C_{12}H_{12}N_2OS_2$, in the above procedure gives a more sensitive end point and can therefore be used for greater accuracy for low concentrations of cyanide. For still lower concentrations of cyanide (less than 0.2 ppm), the selective or specific ion electrode can be employed; this has the added advantage of functioning in colored or dirty solutions (see ELECTROANALYTICAL TECHNIQUES).

The sodium carbonate content may be determined on the same sample after a slight excess of silver nitrate has been added. An excess of barium chloride solution is added and, after the barium carbonate has settled, it is filtered, washed, and decomposed by boiling with an excess of standard hydrochloric acid. The excess of acid is then titrated with standard sodium hydroxide solution, using methyl red as indicator, and the sodium carbonate content is calculated.

Sulfide content is determined by titration with standard lead nitrate solution (1 g/L). The titration is continued until a drop of the test solution on a filter paper ceases to produce a stain with a drop of lead nitrate solution.

Other ions, eg, ferrate, chloride, and formate, are determined by first removing the cyanide ion at ca pH 3.5 (methyl orange end point). Iron is titrated, using thioglycolic acid, and the optical density of the resulting pink solution is measured at 538 nm. Formate is oxidized by titration with mercuric chloride. The mercurous chloride produced is determined gravimetrically. Chloride ion is determined by a titration with 0.1 *N* silver nitrate. The end point is determined electrometrically.

2.6. Health and Safety Factors. Handling, storage, and the use of the alkali metal cyanides must be carried out by trained people. Most serious injuries and fatalities have been caused by inadvertently mixing these cyanides with acids, thereby releasing hydrogen cyanide. All necessary precautions should be taken to prevent cyanide salts from contacting liquid or airborne acids. Avoid storage near, or mixing with, acids. The present threshold limit value for 8-h exposure to cyanide dust is 5 mg/m^3 calculated as CN. Cyanide salts also must be protected from large concentrations of carbon dioxide to avoid hydrogen cyanide liberation. Carbon dioxide fire extinguishers should not be used. Cyanide salts as solids or solutions must be stored in tightly closed containers that must be protected from corrosion or damage. They should be stored so there is no contact with nitrate–nitrite mixtures or peroxides. Storage areas must be adequately ventilated and proper container labeling is mandatory.

Rubber gloves should be worn when handling dry salts. In addition, the following protective items should be used with solution or dusty salts: protective sleeves, aprons, shoes, boots or overshoes made of rubber, chemical safety goggles, full-face shield, and filter-type respirator (where dust is present). Cyanide spills should be flushed to a contained area where treatment to destroy the cyanide can be carried out. Avoid flushing to drains or ditches that may contain acids. In the event that cyanide salts or solutions contact the eyes, they should be flushed for 15 min with a copious, gentle flow of water followed by immediate medical attention. Eating, smoking, and chewing should be forbidden in areas where cyanide salts are handled. Employees should be required to wash carefully after working with cyanide salts and before eating, smoking, or chewing (59).

2.7. Uses. At one time, electroplating was the largest single use for sodium cyanide, especially for zinc (60), copper, brass, and cadmium. Gold, gold alloys, and silver are also plated onto base metals from sodium cyanide solutions. Substantial decline in cyanide electroplating has occurred, however, owing to tighter restrictions on cyanide discharge and conservation of plating and rinse solutions.

Use for heat treating is also small compared to the past. It has been supplanted to a large extent by furnaces using special atmospheric conditions. Heat treatment salts containing sodium cyanide are used for small metal parts when selective case hardening is required.

The principal use of sodium cyanide is for recovery of precious metals. Recovery of gold by cyanidation is the largest single mining use for sodium cyanide and has been growing owing to high gold prices (61). The sodium cyanide, in dilute solution and in the presence of oxygen, is used to dissolve the gold out of the ore. The water-soluble sodium dicyanoaurated(I) [15280-09-8], $NaAu(CN)_2$, is formed. From this dilute solution, a typical process adsorbs the gold complex onto carbon. Then stronger cyanide solutions are used to elute the gold off of the carbon for electrochemical recovery from this solution. Metallic silver frequently occurring with the gold is recovered at the same time.

Chemical uses for sodium cyanide may constitute as much as 5% of the total and are in five general categories: dyes, including optical brighteners (qv); agricultural chemicals; pharmaceuticals; chelating or sequestering agents (see CHELATING AGENTS); and specialties. Sodium cyanide is used in the preparation of nitriles (qv), carbylamines (isonitriles), cyano fatty acids, and heavy metal cyanides (see also CYANOCARBONS). Sodium cyanide reacts with dextrose hydrate in aqueous solution to produce glucoheptonate [31138-65-5] (62). Phenylglycine [109-1-5], the intermediate in the manufacture of indigo [482-89-3], is manufactured using sodium cyanide. Substantial quantities of sodium cyanide are used in sodium ferrocyanide [13601-19-9], $Na_4Fe(CN)_6$, for the manufacture of Prussian blue. Sodium cyanide solution treated with $FeCl_2$ in the presence of alkali metal hydroxide with careful adjustment of pH produces yellow $Na_4Fe(CN)_6$ (63). Sodium cyanide is used to produce sodium nitrilotriacetate [10042-84-9], SNTA, which is an increasingly popular chelating agent as well as a phosphate replacement in certain areas of the world. Cyanuric chloride [108-77-0] is produced in small quantities from sodium cyanide (see CYANURIC AND ISOCYANURIC ACIDS).

Miscellaneous uses for sodium cyanide include heat treating, metal stripping, and compounds used for clearing smut. Treatment of wood chips with sodium cyanide and $CaCl_2$ reportedly increases the kraft cooking yield of pulp (qv) (64).

3. Potassium Cyanide

3.1. Introduction. Potassium cyanide [151-50-8], KCN, a white crystalline, deliquescent solid, was initially used as a flux, and later for electroplating, which is the single greatest use in the 1990s. The demand for potassium cyanide was met by the ferrocyanide process until the latter part of the nineteenth century, when the extraordinary demands of the gold mining industry for alkali cyanide resulted in the development of direct synthesis processes. When cheaper sodium cyanide became available, potassium cyanide was displaced in many uses. With the decline in the use of alkali cyanides for plating the demand for potassium cyanide continues to decline. The total world production in 1990 was estimated at about 4500 t, down from 7300 t in 1976.

Commercial potassium cyanide made by the neutralization or wet process contains 99% KCN; the principal impurities are potassium carbonate, formate, and hydroxide. To prepare 99.5 + % KCN, high quality hydrogen cyanide and KOH must be used.

3.2. Properties.

Physical Properties. The physical properties of potassium cyanide are given in Table 6. Unlike sodium cyanide, potassium cyanide does not form a dihydrate.

The solubility of potassium cyanide in nonaqueous solvents is as follows: in anhydrous liquid ammonia, 4.55 g/100 g NH_3 at −33.9°C; 4.91 g/100 g methanol at 19.5°C; 0.57 g/100 g ethanol at 19.5°C; 146 g/L solution in formamide at 25°C; 41 g/100 g hydroxylamine at 17.5°C; 24.24 g/100 g glycerol of specific gravity 1.2561 at 15.5°C; 0.73 g/L solution in phosphorus oxychloride at 20°C; 0.017 g/100 g liquid sulfur dioxide at 0°C; and 0.22 g/100 g dimethylformamide at 25°C.

At room temperature, potassium cyanide has fcc crystal structure (65). Average potassium cyanide crystals inherently have three to four times the mass or size of sodium cyanide crystals.

Chemical Properties. Potassium cyanide is readily oxidized to potassium cyanate [590-28-3] by heating in the presence of oxygen or easily reduced oxides, such as those of lead or tin or manganese dioxide, and in aqueous solution by reaction with hypochlorites or hydrogen peroxide.

Dry potassium cyanide in sealed containers is stable for many years. An aqueous solution of potassium cyanide is slowly converted to ammonia and

Table 6. **Physical Properties of Potassium Cyanide**

Property	Value
molecular weight	65.11
melting point, °C	634
density, g/mL	
cubic	1.55
orthorhombic at −60°C	1.62
specific heat, 25–72°C, J/g[a]	1.01
heat of fusion, J/mol[a]	14.7×10^3
heat of formation, ΔH_f°, J/mol[a]	-113×10^3
heat of solution, ΔH_{soln}, J/mol[a]	−12550
hydrolysis constant, 25°C	2.54×10^{-5}
solubility at 25°C, g/100 g H_2O	71.6
resistivity, Ω · cm	
0.25 *N* soln	70
0.5 *N* soln	15
1.0 *N* soln	10
2.0 *N* soln	5

[a] To convert J to cal, divide by 4.184.

potassium formate; the decomposition rate accelerates with increasing temperature. However, at comparable temperatures the rate of conversion is far lower than that for sodium cyanide; only about 25% as great.

Many reactions can be carried out between potassium cyanide and organic compounds with the alkalinity of the KCN acting as a catalyst; these reactions are analogous to reactions of sodium cyanide. The reactions of potassium cyanide with sulfur and sulfur compounds are also analogous to those of sodium cyanide. Potassium cyanide is reduced to potassium metal and carbon by heating it out of contact with air in the presence of powdered magnesium. Magnesium is converted to the nitride:

$$2\ \mathrm{KCN} + 3\ \mathrm{Mg} \longrightarrow 2\ \mathrm{K} + 2\ \mathrm{C} + \mathrm{Mg_3N_2}$$

Beryllium, calcium, boron, and aluminum act in a similar manner. Malonic acid is made from monochloroacetic acid by reaction with potassium cyanide followed by hydrolysis. The acid and the intermediate cyanoacetic acid are used for the synthesis of polymethine dyes, synthetic caffeine, and for the manufacture of diethyl malonate, which is used in the synthesis of barbiturates. Most metals dissolve in aqueous potassium cyanide solutions in the presence of oxygen to form complex cyanides (see COORDINATION COMPOUNDS).

3.3. Manufacture. Potassium cyanide was made by the Beilby process before the introduction of the neutralization or wet process. In the Beilby process, cyanide is made according to the following overall reaction:

$$\mathrm{K_2CO_3} + 4\ \mathrm{C} + 2\ \mathrm{NH_3} \longrightarrow 2\ \mathrm{KCN} + 3\ \mathrm{CO} + 3\ \mathrm{H_2}$$

In this dry process, ammonia gas passes into a molten mixture of potassium carbonate and charcoal. Although purity of the product is high, this process became obsolete because of the lower costs of the neutralization process.

Potassium cyanide is manufactured by the reaction of an aqueous solution of potassium hydroxide and hydrogen cyanide:

$$\mathrm{KOH} + \mathrm{HCN} \longrightarrow \mathrm{KCN} + \mathrm{H_2O}$$

The cyanide, which crystallizes in the anhydrous state from aqueous solution, is recovered by evaporation under reduced pressure, filtration, and drying. Because the crystal size is significantly larger than sodium cyanide it can be sold in powder form without excessive dusting. However, it tends to cake in the shipping container and is often compacted and granulated to larger sizes.

3.4. Uses. Potassium cyanide is primarily used for fine silver plating but is also used for dyes and specialty products (see ELECTROPLATING). Electrolytic refining of platinum is carried out in fused potassium cyanide baths, in which a separation from silver is effected. Potassium cyanide is also a component of the electrolyte for the analytical separation of gold, silver, and copper from platinum. It is used with sodium cyanide for nitriding steel and also in mixtures for metal coloring by chemical or electrolytic processes.

Potassium cyanide like sodium cyanide, is shipped in steel or fiber drums. Potassium cyanide costs more than sodium cyanide, primarily because of the higher price of potassium hydroxide. The 1991 price was $3.88/kg.

4. Other Cyanides

4.1. Lithium, Rubidium, and Cesium Cyanides. Lithium cyanide [2408-36-8], rubidium cyanide [19073-56-4], and cesium cyanide [21159-32-0] are white or colorless salts, isomorphous with potassium cyanide. In physical and chemical properties these cyanides closely resemble sodium and potassium cyanide. As of this writing these cyanides have no industrial uses.

All of these alkali metal cyanides may be prepared by passing hydrogen cyanide into an aqueous solution of the hydroxide or by precipitating a solution of barium cyanide [542-62-1] with lithium, rubidium, or cesium sulfate. A product with fewer contaminants may be obtained by the reaction of the base in absolute alcohol or dry ether with anhydrous hydrogen cyanide (66). In another method of preparation, a suspension of rubidium, cesium, or lithium metals in anhydrous benzene is treated with anhydrous hydrogen cyanide, and the benzene subsequently removed by evaporation under reduced pressure.

These cyanides are all soluble in water. The cyanide ion is weakly held so that water solutions have a much stronger odor of hydrogen cyanide above them than sodium and potassium cyanide solution.

Lithium cyanide melts at 160°C. In the fused state the specific gravity at 18°C is 1.075. It is highly hygroscopic. Rubidium cyanide is not hygroscopic and is insoluble in alcohol or ether. Cesium cyanide is highly hygroscopic.

Lithium cyanide decomposes to cyanamide and carbon below about 600°C. This decomposition is similar to the alkaline-earth cyanides (67). Iron accelerates decomposition and, when heated with 10% iron at 500°C for 15 h, lithium cyanide is completely converted to lithium cyanamide [2408-36-8].

4.2. Ammonium Cyanide. Ammonium cyanide [12211-52-8], NH_4CN, a colorless crystalline solid, is relatively unstable, and decomposes into ammonia and hydrogen cyanide at 36°C. Ammonium cyanide reacts with ketones (qv) to yield aminonitriles. Reaction of ammonium cyanide with glyoxal produces glycine. Because of its unstable nature, ammonium cyanide is not shipped or sold commercially. Unless it is kept cool and dry, decomposition releases vapors and forms black hydrogen cyanide polymer.

Ammonium cyanide may be prepared in solution by passing hydrogen cyanide into aqueous ammonia at low temperatures. It may also be prepared from barium cyanide and ammonium sulfate, or calcium cyanide with ammonium carbonate. It may be prepared in the dry state by gently heating a mixture of potassium cyanide or ferrocyanide and ammonium chloride, and condensing the vapor in a cooled receiver. Ammonium cyanide is soluble in water or alcohol. The vapor above solid NH_4CN contains free NH_3 and HCN, a very toxic mixture.

4.3. Calcium Cyanide. Crude calcium cyanide [592-01-8], about 48 to 50 eq% sodium cyanide, is the only commercially important alkaline-earth metal cyanide, and output tonnage has been greatly reduced. This product, commonly called black cyanide, is marketed in flake form as a powder or as cast blocks under the trademarks Aero and Cyanogas of the American Cyanamid Co.

The calcium cyanamide process was first discovered in Germany in the early 1900s during experimental attempts to produce cyanide cheaply (68,69). Following the discovery, the best attempts resulted in only 17.5% sodium cyanide equivalent product. Because of a shortage of cyanide in the United States in 1916, the American Cyanamid Co. developed a batch process giving higher yields that evolved into a continuous electric-furnace process in 1919. Subsequent improvements increased the strength to 48 to 50% sodium cyanide equivalent. Calcium cyanide solutions of about 15% concentration have been prepared for use in gold extraction in South Africa from hydrogen cyanide and lime.

Properties. Because of decomposition, the melting point of calcium cyanide can only be estimated by extrapolation to be 640°C (70).

Calcium cyanide diammoniate [69365-88-4], $Ca(CN)_2 \cdot 2NH_3$, is formed in liquid ammonia by reaction of calcium hydroxide or nitrate with ammonium cyanide. Deammoniation under heat and high vacuum yields calcium cyanide, a white powder, which is readily hydrolyzed to hydrogen cyanide. The diammoniate is more stable than the cyanide containing no ammonia. Calcium cyanide can be made by passing ammonia and hydrogen cyanide over calcium hydroxide. A compound having even higher cyanide content is obtained by subjecting calcium carbide (see Carbides) to the action of liquid hydrogen cyanide in the presence of 0.5–5% of water; it has also been formed in a nonaqueous medium such as dimethylformamide. These processes are distinct from those for the fused cyanides in which nitrification of calcium carbide yields calcium cyanamide [156-62-7], which in turn produces calcium cyanide by reaction with carbon.

Aqueous solutions of calcium cyanide prepared even at low temperature turn yellow or brown owing to the formation of HCN polymer. Calcium cyanide hydrolyzes readily.

$$\mathrm{Ca(CN)_2 + 2\ H_2O \longrightarrow 2\ HCN\ black\ polymer + Ca(OH)_2}$$

The presence of brown polymer in solid form is sometimes noted even in dry calcium cyanide that has been stored for long periods. Calcium cyanide is decomposed by carbon dioxide, acids, and acidic salts liberating hydrogen cyanide.

Ferrocyanides are produced by reaction of ferrous salts

$$\mathrm{3\ Ca(CN)_2 + FeSO_4 \longrightarrow Ca_2\left[Fe(CN)_6\right] + CaSO_4}$$

With sulfur in aqueous medium, calcium cyanide forms calcium thiocyanate [2092-16-2]

$$\mathrm{Ca(CN)_2 + 2\ S \longrightarrow Ca(SCN)_2}$$

Manufacture. Calcium cyanide is made commercially from lime [1305-78-3], CaO, coke, and nitrogen. The reactions are carried out in an electric furnace (69).

$$\mathrm{CaO + 3\ C \xrightarrow{2200^\circ C} CaC_2 + CO}$$

$$\mathrm{CaC_2 + N_2 \xrightarrow{1500^\circ C} CaNCN + C}$$

$$\mathrm{CaNCN + C \xrightarrow[1000^\circ C]{N_2Cl} Ca(CN)_2}$$

Table 7. **Typical Analysis of Calcium Cyanide**

Constituent	Concentration, wt%
$Ca(CN)_2$	45–50
NaCl	32
CaO	12
graphite	1–2
CaC_2	2–3
CaNCN	2.5
SiO_3	0.9
$M_2O_3 + Al_2O_3$	2.3[a]
CaS	0.4
CaF	0.5
MgO	0.3

[a] M may be Fe, Cr, or less commonly Ni, Co, or other metals.

The resulting melt is cooled rapidly to prevent reversion to calcium cyanamide. The product is marketed in the form of flakes, dark gray because of the presence of carbon. Typical composition is shown in Table 7. Because the rate of hydrogen cyanide evolution is relatively high, it is readily adaptable to fumigation. Specific gravity of the product is 1.8 to 1.9. The price of black cyanide is generally lower than sodium cyanide; it is manufactured in Canada and South Africa.

Safety Precautions. Precautions similar to those used for sodium cyanide should be used for black cyanide. Contact with acidic compounds generates hydrogen cyanide gas. Some additional precaution must be taken to minimize contact with water or even the humidity of the atmosphere because decomposition and hydrogen cyanide evolution occurs. Black cyanide is shipped in steel drums and is designated as a Class B poison. It is extremely toxic to humans, animals, and fish. Ingestion, contact with the skin, inhalation of the dust or hydrogen cyanide evolved should be avoided. Black cyanide should be stored in tight containers under moisture-free conditions; the small amount of contained carbide can evolve acetylene. Adequate ventilation and protective equipment similar to that for sodium cyanide should be provided in handling the solid cyanide and in the preparation of aqueous solutions.

Uses. The extraction or cyanidation of precious metal ores was the first, and is still the largest, use for black cyanide (71). The leaching action of the cyanide results from the formation of soluble cyanide complexes.

$$4\ Ag + 4\ Ca(CN)_2 + O_2 + 2\ H_2O \longrightarrow 2\ Ca\left[Ag(CN)_2\right]_2 + 2\ Ca(OH)_2$$

This reaction also applies to gold.

The flake cyanide is dissolved and added to suspensions of finely ground ore under agitation and in the presence of air. The dissolved gold and silver are precipitated by the addition of zinc dust and the crude precipitate is refined to produce bullion.

Black cyanide is also used in the processes in which the gold complexes are adsorbed on carbon. To recover the gold from the carbon a more concentrated solution of sodium cyanide is used.

The use of black cyanide as a fumigant and rodenticide makes use of the atmospheric humidity action that liberates hydrogen cyanide gas. It can only be used effectively in confined spaces where hydrogen cyanide builds up to lethal concentrations for the particular application. Black cyanide is also used in limited quantities in the production of prussiates or ferrocyanides (see IRON COMPOUNDS).

4.4. Other Alkaline-Earth Cyanides. Magnesium cyanide [22400-99-3], $Mg(CN)_2$, may be formed by reaction of finely divided magnesium metal and ammonium cyanide in liquid ammonia. Removal of the ammonia yields a white solid, magnesium cyanide diammoniate [69309-45-1]; deammoniation by heating under vacuum gives the cyanide, which is similar in properties to calcium cyanide. Strontium cyanide [60448-24-0] and barium cyanide [60448-23-9]are somewhat more stable than calcium and magnesium cyanides and their preparation is by reaction of strontium or barium hydroxide and hydrogen cyanide in water followed by low temperature evaporation under vacuum. The cyanides of magnesium, barium, and strontium have not been marketed.

BIBLIOGRAPHY

"Cyanides and Cyanogen Compounds" in *ECT* 1st ed., Vol. 4, pp. 689–712, by W. J. Miller and D. E. Nye, E.I. du Pont de Nemours & Co., Inc., and R. B. Mooney, American Cyanamid Co., "Hydrogen Cyanide" under "Cyanides" in *ECT* 2nd ed., Vol. 6, pp. 574–585, by P. D. Montgomery, Monsanto Co.; "Cyanides (Alkali Metal)" under "Cyanides" in *ECT* 2nd ed., Vol. 6, pp. 585–601, by R. B. Mooney and J. P. Quin, Imperial Chemical Industries Ltd; "Alkaline-Earth Metal Cyanides" under "Cyanides" in *ECT* 2nd ed., Vol. 6, pp. 601–704, by R. B. Booth, American Cyanamid Co.; "Cyanides" in *ECT* 3rd ed., Vol. 7, pp. 307–334, by W. R. Jenks, E.I. du Pont de Nemours & Co., Inc.; in *ECT* 4th ed., Vol. 7, pp. 753–782, by Lawrence D. Pesce, E. I. du Pont de Nemours & Co., Inc.

CITED PUBLICATIONS

1. C. Ponnamperuma, *Sci. J.* **1**(3), 39045 (1965).
2. J. P. Ferris *Science* **203**, 1135 (1979); C. N. Matthews, *Science* **203**, 1136 (1979).
3. R. J. Cicerone and R. Zellner, *J. Geophys. Res.* **88**(C15), 10689 (1983).
4. A. W. Cobb and J. H. Walton, *J. Chem. Phys.* **41**, 351 (1957).
5. S. Barrett and A. F. Titley, *J. Chem. Soc.* **115**, 902 (1919).
6. A. Bernthsen, *Ann.* **192**, 1 (1878).
7. U.S. Pat. 2,712,493 (July 5, 1955), W. Moje (to E.I. du Pont de Nemours & Co., Inc.).
8. Ger. Pat. 1,056,101 (Apr. 30, 1959), H. Zima (to Rohm & Haas GmbH).
9. U.S. Pat. 2,672,398 (Mar. 16, 1954), H. Huemer, H. Schulz, and W. Pohl (to Deutsche Gold und Silber-Scheideanstalt).
10. R. Oleinek, *Rev. Chim.* **16**, 19 (1965).
11. U.S. Pat. 2,399,361 (Apr. 30, 1946), B. S. Lacy and W. S. Hinegardner (to E.I. du Pont de Nemours & Co., Inc.).
12. U.S. Pat. 2,762,798 (Sept. 11, 1956), N. L. Hardwicke and G. W. Walpert (to Monsanto Co.).
13. U.S. Pat. 2,434,606 (Jan. 13, 1948), E. L. Carpenter (to American Cyanamid Co.).
14. G. Schlesinger and S. L. Miller, *J. Am. Chem. Soc.* **95**, 3729 (1973).

15. L. I. Krimen and J. Donald, *Org. React* **17**, 213 (1969).
16. Can. Pat. 902,099 (Apr. 26, 1971), H. Neumaier and co-workers (to Knapsack Aktiengesellschaft).
17. Ger. Pat., 2,205,983 (Aug. 16, 1973), W. Gruber and co-workers (to Röhm GmbH).
18. U.S. Pat. 3,177,215 (Apr. 6, 1965), R. W. Foreman and co-workers (to Standard Oil Co.).
19. U.S. Pat. 3,988,360 (Oct. 26, 1976), R. Gaudette and J. Philbrook (to W. R. Grace & Co.).
20. R. C. Sheridan and E. H. Brown, *J. Org. Chem* **30**(2), 668 (1965).
21. Jpn. Pat. 7,404,207 (Jan. 31, 1974), Y. Hamamoto (to Kyowa Gas Chemical Industry Co., Ltd.).
22. U.S. Pat. 3,666,787 (May 30, 1972), O. Webster (to E.I. du Pont de Nemours & Co., Inc.).
23. U.S. Pat. 1,934,838 (Nov. 14, 1933), L. Andrussow (to I. G. Farbenindustrie, AG).
24. L. Andrussow, *Agnew. Chem.* **48**, 593 (1935).
25. L. Andrussow, *Bull. Soc. Chim. Fr.* **18**, 45 (1951).
26. L. Andrussow, *Chem. Ing. Tech.* **27**, 469 (1955).
27. L. Andrussow, *Chim. Ind. Genie Chim.* **86**, 39 (1961).
28. C. T. Kautter and W. Leitberger, *Chem. Ing. Tech.* **25**, 599 (1953).
29. P. W. Sherwood, *Pet. Eng.* **31**, C-22, C-51 (1959).
30. U.S. Pat. 3,215,495 (Nov. 2, 1965), W. R. Jenks and A. W. Andresen (to E.I. du Pont de Nemours & Co., Inc.).
31. U.S. Pat. 3,360,355 (Dec. 26, 1967), W. R. Jenks (to E.I. du Pont de Nemours & Co., Inc.).
32. U.S. Pat. 3,104,945 (Sept. 24, 1963), W. R. Jenks and R. M. Shepherd (to E.I. du Pont de Nemours & Co., Inc.).
33. R. Rodiger, *Chem. Tech. (Berlin)* **10**, 135 (1958).
34. F. Endter, *Chem. Ing. Tech.* **30**, 305 (1958).
35. *Chem. Week* **83**(4), 70 (1958).
36. Ger. Pat. 2,014,523 (Apr. 17, 1970) (to Degussa).
37. N. B. Shine, *Chem. Engr. Prog.* **67**, 2 (1971).
38. G. E. Johnson and co-workers, *U.S. Bureau of Mines Report*, No. RI6994, Washington, D.C., 1967.
39. Ital. Pat. 845,992 (July 2, 1969) (to Montecatini Edison).
40. R. J. H. Voorhoeve and co-workers, *J. Catal.* **45**, 297 (1976).
41. Ger. Pat. 1,143,497 (Feb. 14, 1963), G. Schulze and G. Weiss (to Badische Anilin-und Soda-Fabrik AG).
42. D. Hasenberg, *HCN Synthesis on Polycrystalline Platinum and Rhodium*, dissertation, University of Minnesota, 1984.
43. U.S. Pat. 2,797,148 (June 25, 1957), H. C. Carlson (to E.I. du Pont de Nemours & Co., Inc.).
44. E. Koberstein, *Ind. Eng. Chem. Process Des. Dev.* **12**(4) (1973).
45. H. Roos and M. Schmidt, *Chem. Ing. Tech.* **49**, 369 (1977).
46. J. L. Huiatt and co-workers, eds., *Proceedings of a Workshop—Cyanide From Mineral Processing*, University of Utah, Salt Lake City, 1982.
47. T. Green, *The Prospect for Gold*, Walker Publishing Co. Inc., 1987.
48. E. D. Oliver and S. E. J. Johnson, *J. Am. Chem. Soc.* **76**, 4721 (1954).
49. V. A. Kireev and L. I. Vogranskaya, *J. Gen. Chem. USSR* **5**, 963 (1935).
50. U.S. Pat. 2,949,341 (Aug. 16, 1960), C. P. Green (to E.I. du Pont de Nemours & Co., Inc.).
51. E. Rishkevich, *Z. Electrochem.* **39**, 531 (1933).
52. E. W. Guernsey and M. S. Sherman, *J. Am. Chem. Soc.* **48**, 695 (1926).

53. R. Holtze, *A. Anorg. Allgem. Chem.* **214**, 65 (1933).
54. B. Ricca and G. D'Amore, *Gazz. Chim. Ital.* **79**, 308 (1949).
55. U.S. Pat. 2,993,754 (July 25, 1961), W. R. Jenks and J. S. Linder (to E.I. du Pont de Nemours & Co., Inc.).
56. U.S. Pat. 3,619,132 (Nov. 9, 1971), H. J. Mann and co-workers (to Degussa).
57. U.S. Pat. 2,944,344 (July 12, 1960), C. P. Green and W. R. Jenks (to E.I. du Pont de Nemours & Co., Inc.).
58. U.S. Pat. 3,615,176 (Oct. 26, 1971), W. R. Jenks and O. W. Shannon (to E.I. du Pont de Nemours & Co., Inc.).
59. *Sodium Cyanide Material Safety Data Sheet*, E.I. du Pont de Nemours & Co., Inc., Wilmington, Del., 1990.
60. H. Geduld, *Metal Finish* **74**(1), 45 (1976).
61. M. C. Fuerstenau and J. L. Hendrix, eds., *Advances in Gold and Silver Processing Proceedings*, Society for Mining, Metallurgy, & Exploration, Inc., Littleton, Colo., 1990.
62. U.S. Pat. 3,679,659, (July 25, 1972), C. Zak (to Belzak Corp.).
63. U.S. Pat. 3,695,833 (Oct. 3, 1972), O. Wiedeman and co-workers (to American Cyanamid Co.).
64. U.S. Pat. 3,883,391 (May 13, 1975), R. B. Phillips (to International Paper Co.).
65. R. M. Bozorth, *J. Am. Chem. Soc.* **44**, 317 (1922).
66. J. Meyer, *Z. Anorg. Allgem. Chem.* **115**, 203 (1920).
67. A. Perret and J. Riethmann, *Helv. Chim Acta* **26**, 740 (1943).
68. U.S. Pat. 776,314 (Nov. 29, 1904), A. Frank.
69. *Mining Chemicals Handbook*, American Cyanamid, Wayne, N.J., 1986.
70. G. Peterson and H. H. Franck, *Z. Anorg. Allgem. Chem.* **237**, 1 (1938).
71. J. V. N. Dorr and F. L. Bosqui, *Cyanidation and Concentration of Gold and Silver Ores*, McGraw-Hill Book Co., Inc., New York, 1950.

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