

# Cyano Compounds, Inorganic

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## 1. Hydrogen Cyanide

Hydrogen cyanide [74-90-8], hydrocyanic acid, prussic acid, formonitrile, HCN,  $M_r$  27.03, is a colorless liquid with the characteristic odor of bitter almonds. Hydrogen cyanide in aqueous

solution was first prepared by SCHEELÉ in 1782 [22]. The acid occurs naturally in combination with some glucosides, such as amygdalin.

Hydrogen cyanide is currently produced by direct reaction of alkanes with ammonia, and indirectly as a byproduct of the manufacture of

acrylonitrile (by ammoxidation of propene → Acrylonitrile). Major end uses include the production of adiponitrile, methyl methacrylate, cyanuric chloride, chelating agents, sodium cyanide, and methionine and its hydroxy analogues.

## 1.1. Properties

### Physical Properties [1, 23–26]:

Melting point	−13.24 °C
Boiling point	25.70 °C
Vapor pressure	
at 0 °C	35 kPa
at 20 °C	83 kPa
at 50 °C	250 kPa
Enthalpy of formation (HCN liquid), $\Delta H$	3910 kJ/kg
Critical temperature	183.5 °C
Critical density	0.20 g/cm <sup>3</sup>
Critical pressure	5 MPa (50 bar)
Density (20 °C)	0.687 g/cm <sup>3</sup>
Specific heat, liquid (20 °C)	2630 J kg <sup>−1</sup> K <sup>−1</sup>
Specific heat, gas (25 °C)	1630 J kg <sup>−1</sup> K <sup>−1</sup>
Heat of fusion	310 kJ/kg
Heat of vaporization	935 kJ/kg
Heat of polymerization	−1580 kJ/kg
Explosive range in air	5.5 – 46.5 vol %
Flash point	−17.8 °C
Ignition temperature	535 °C
Dynamic viscosity, $\eta$ (20 °C)	0.192 mPa · s
Surface tension (20 °C)	18.33 mN/m
Dielectric constant	
at 0 °C	158.1
at 20 °C	114.9
Dissociation constant	
aqueous solution, pK (20 °C)	9.36

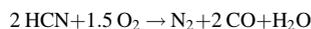
As a result of its high dielectric constant, HCN has acquired some importance in preparative chemistry as a nonaqueous, ionizing solvent [27].

**Chemical Properties.** Some comprehensive reviews on hydrogen cyanide and cyanogen compounds have been published [1–3]. The acid occurs only in the nitrile form. Although isomeric isonitrile HNC has been detected in interstellar space, all efforts to isolate this compound have failed. As the nitrile of formic acid, HCN undergoes many typical nitrile reactions. For example, hydrogen cyanide can be hydrolyzed to formic acid by aqueous sulfuric acid or hydrogenated to methylamine. Hydrogen cyanide adds to carbon – carbon double bonds and forms cyanohydrins with carbonyl groups of aldehydes or ketones. The most important uses of this type are

in the manufacture of acetone cyanohydrin (an intermediate in the production of methyl methacrylate) and in the production of adiponitrile from butadiene and hydrogen cyanide. Another example is the multistep synthesis of amino acids via hydantoins. Hydrogen cyanide can be oxidized by air over silver or gold catalysts at 300 – 650 °C to yield cyanic acid (HOCN) and cyanogen (CN)<sub>2</sub> in an approximate 2/1 ratio.

The reaction of hydrogen cyanide with chlorine gives cyanogen chloride (see Section 4.2). For industrial purposes, the latter compound is usually directly trimerized to cyanuric chloride, the starting material for the chemistry of *s*-triazines.

In the presence of oxygen or air, hydrogen cyanide burns with a very hot flame. For the reaction



the heat of formation is calculated to be −723.8 kJ/mol and the adiabatic flame temperature is 2780 °C. Pure liquid or gaseous HCN is inert to most metals and alloys such as aluminum, copper, silver, zinc, and brass. At higher temperatures (> 600 °C), the acid reacts with metals that can form carbides and nitrides (titanium, zirconium, molybdenum, and tungsten).

Pure liquid hydrogen cyanide has a tendency to polymerize to brown-black, amorphous polymers, commonly called azulmic acid [26746-21-4]. The reaction is accelerated by basic conditions, higher temperature, UV light, and the presence of radicals. Since the decomposition is exothermic, the polymerization reaction is autocatalytic and can proceed with explosive violence to form the HCN dimer iminoacetonitrile [1726-32-5] and the HCN tetramer diaminomaleonitrile [1187-42-4] as intermediates [28, 29]. Both compounds are presumed to be important in the evolution of life, and cyano compounds may play a role in prebiotic syntheses [30, 31]. In the liquid phase, hydrogen cyanide is stabilized by the presence of small amounts of acids (0.1 wt % H<sub>3</sub>PO<sub>4</sub>, 1 – 5 % HCOOH or CH<sub>3</sub>COOH) or 0.2 wt % SO<sub>2</sub> in the gas phase.

**The HCN – H<sub>2</sub>O System.** At 25 °C, hydrogen cyanide is miscible with water in all ratios. The solution is a weak acid, with a dissociation constant of the same order of magnitude as amino

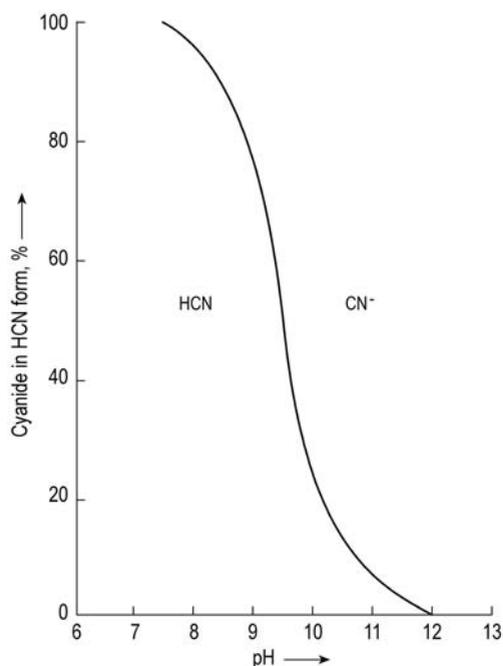


Figure 1. HCN/CN<sup>-</sup> equilibrium as a function of pH

acids. The relation between total cyanide concentration ( $c_{\text{HCN}} + c_{\text{CN}^-}$ ) and dissociated cyanide ( $c_{\text{CN}^-}$ ) in a dilute aqueous solution, as a function of pH, is illustrated in Figure 1.

Figure 2 shows the liquid – vapor equilibrium diagram at atmospheric pressure. Because of the high HCN partial vapor pressure it is

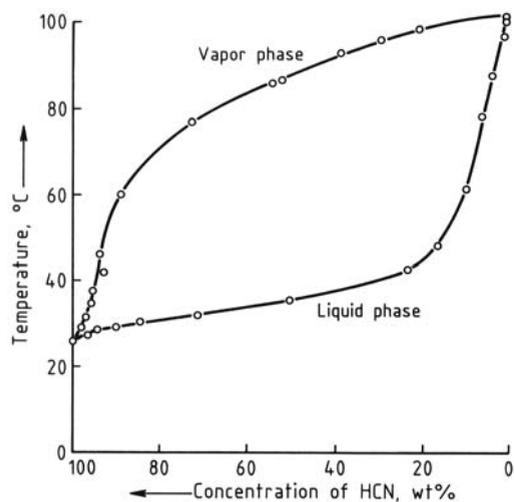


Figure 2. Liquid – vapor diagram of the system H<sub>2</sub>O – HCN at atmospheric pressure

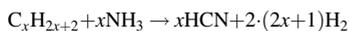
difficult to separate the acid from a gas mixture by absorption in water, which is an important consideration for industrial practice [32].

The stability of hydrogen cyanide solutions depends on the degree of dilution: at concentrations below 0.1 mol/L HCN, the acid is stable; addition of traces of acid prevents decomposition. Like pure HCN, the exothermic polymerization of an aqueous solution is accelerated by the presence of alkali. In addition to azulmic derivatives, small amounts of amino acids and purine bases are formed. This fact is of some importance to biological chemistry. The C≡N triple bond is hydrolyzed by strong alkali or acid to give formic acid and ammonia. Higher temperatures or hydrothermal conditions favor these reactions.

## 1.2. Production [1, 33, 34]

Hydrogen cyanide can be produced when sufficient energy is supplied to any system containing the elements hydrogen, nitrogen, and carbon. Generally, only processes starting from hydrocarbons and ammonia are of economic importance today; however, the production of hydrogen cyanide from formamide [35] is carried out in a plant at Ludwigshafen, Germany and since 1997 in a plant in Niigata, Japan. Alternative raw materials such as methanol, carbon, or carbon monoxide [36–45] are of interest since the 1980s. The ammoxidation of methanol to HCN is performed in Japan in a 10 000 – 15 000 t/a plant.

These routes can compete with conventional technology given specific site conditions. The reaction of hydrocarbons with ammonia



is highly endothermic and needs a continuous heat supply. The means of providing this energy requirement are manifold and characteristic of the different processes [47]. Direct microwave heating of the catalyst has been developed for small-scale local synthesis of HCN [48]. The main processes currently used to make hydrogen cyanide: the Andrussov ammoxidation process, which involves the reaction of ammonia, methane, and air over a catalyst gauze; and the two ammonia dehydration routes, the methane – ammonia (BMA) and the Shawinigan processes,

developed by Degussa and Gulf Oil Company, respectively. The latter are performed in externally heated ceramic tubes or in an electrically heated fluidized coke bed. Twenty-five percent of the hydrogen cyanide in the United States and 20% in Western Europe is obtained as a byproduct in the manufacture of acrylonitrile by the oxidation of propene in the presence of ammonia (Sohio technology).

### 1.2.1. Andrussow Process

The Andrussow process was developed around 1930 by L. ANDRUSSOW of I.G. Farben [49–51] and is the most widely used method for direct synthesis of hydrogen cyanide. The average capacity of single commercial installations is  $(5 - 30) \times 10^3$  t/a; large plants are operated by DuPont, Rohm and Haas, Novartis and Cyanco in the United States; ICI, Butachemie, Röhm and Elf-Atochem in Western Europe; and Mitsubishi Gas in Japan.

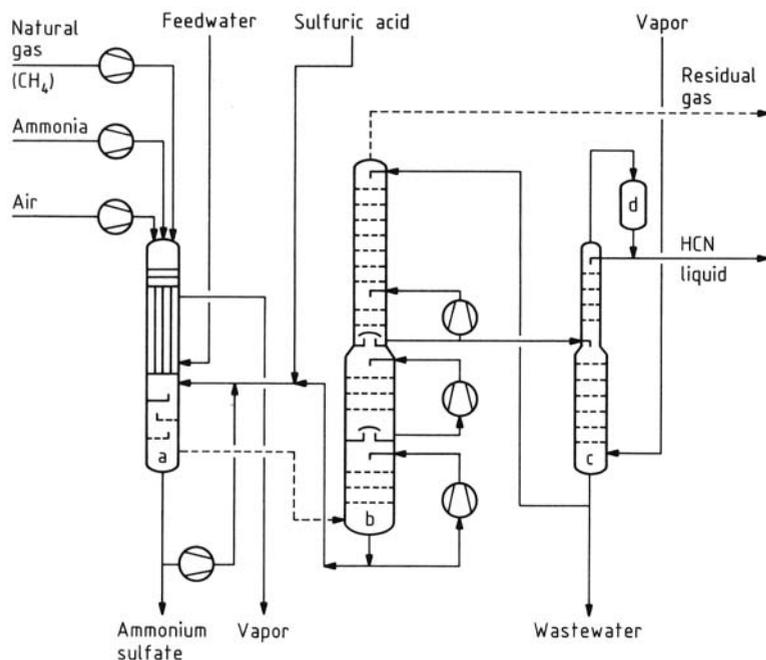
Figure 3 is a flow diagram of the Andrussow process. Natural gas, essentially sulfur-free methane, is mixed with ammonia. Compressed

air is added in a volume ratio that corresponds closely to the theoretical reaction [52]:



The mixture is passed over a platinum – rhodium or platinum – iridium gauze [53] catalyst; temperature and upper flammability limit should be monitored carefully [54, 55]. The reaction takes place at  $> 1000$  °C, at around atmospheric pressure, and with a gas velocity through the catalyst zone of about 3 m/s. To avoid decomposition of HCN, the effluent gas from the reactor is quickly cooled in a waste-heat boiler, which produces the steam used in the process.

After the waste-heat boiler, the gas is washed with dilute sulfuric acid to remove unreacted ammonia; this is necessary to prevent polymerization of HCN. Because disposal of the resulting ammonium sulfate solution is expensive, other systems have been patented [56–58]. Alternatively, the off-gas from the reactor is passed through a monoammonium phosphate solution [59, 60], which converts the ammonia to diammonium phosphate. To effect thermal reversal of the phosphate equilibrium, the absorption solution is



**Figure 3.** Simplified diagram of the Andrussow process  
a) Reactor and ammonia scrubber; b) HCN absorption tower; c) HCN rectifier; d) Condenser

boiled in a stripper by injection of steam. The released ammonia is condensed and recycled to the reactor, while the regenerated monoammonium phosphate solution is pumped back to the absorber.

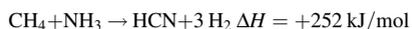
After the ammonia scrubber, the gas is passed through a countercurrent column in which the hydrogen cyanide is absorbed in cold water and the resulting solution is stabilized by adding acid (ca. 0.1 %). The hydrogen cyanide is stripped from the aqueous solution in a rectifier and condensed. The end product is highly pure and has a water content of less than 0.5 %. The aqueous absorber solution, containing traces of HCN, is cooled and fed back to the absorption tower. The residual gases, H<sub>2</sub>, CO, and N<sub>2</sub>, can be used for heating or methanated in a separate unit and recycled as feedstock for HCN manufacture [61].

The advantages of the Andrussow process include (1) long catalyst life, up to 10 000 h; (2) well-tested technology, with a simple and safe reaction system; and (3) high-purity HCN. A disadvantage is that the process is dependent on pure methane as a raw material to avoid carburization of the platinum catalyst; for example, a small percentage of higher hydrocarbon impurities rapidly causes problems with the catalyst system and reduces conversion rates. Other important poisons for platinum are sulfur and phosphorus compounds. A further problem is the relatively low yield based on methane (60 – 70 %) and ammonia (70 %), as well as the low hydrogen cyanide concentration in the product gas, so that recovery equipment must handle large volumes of gas.

The compositions of reaction and residual gases in the Andrussow and BMA processes are compared in Table 1.

### 1.2.2. Methane – Ammonia (BMA) Process

The basis of the Degussa BMA process is the formation of hydrogen cyanide in the absence of oxygen [62–66]. The reaction



is endothermic, requires temperatures above 1200 °C, and is performed in externally heated, alumina tube bundles, which are coated with a thin layer of a special platinum catalyst [67, 68].

**Table 1.** Composition of off-gases and residual gases (volume fractions, %) on the basis of pure methane and ammonia in the BMA and Andrussow processes

Compound	BMA		Andrussow*	
	After reaction	Residual	After reaction	Residual
HCN	22.9	<10 <sup>-2</sup>	7.6	<10 <sup>-2</sup>
NH <sub>3</sub>	2.5	<10 <sup>-2</sup>	2.3	> 0
H <sub>2</sub>	71.8	96.2	13.3	14.7
N <sub>2</sub>	1.1	1.5	49.2	54.6
CH <sub>4</sub>	1.7	2.3	0.3	0.4
CO			3.8	4.2
H <sub>2</sub> O			23.1	25.7
CO <sub>2</sub>			0.4	0.4

\* Calculated because no consumption figures are available.

Several of these bundles are fixed in a reaction furnace unit. A mixture of ammonia and methane (natural or refined gas with a content of 50 – 100 vol % methane) is passed through the tubes and quickly heated to 1300 °C at normal pressure. To avoid the formation of any disturbing deposits of carbon black, the NH<sub>3</sub>/CH<sub>4</sub> ratio is kept between 1.01 and 1.08. After leaving the reaction tubes, the product gas is cooled to 300 °C by passage through a water-cooled aluminum chamber. A kinetic study has shown that a particular temperature profile is essential for this process [69].

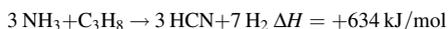
The subsequent reaction steps, ammonia absorption and hydrogen cyanide isolation, are similar to those of the Andrussow process. A distinct advantage is the higher HCN content (Table 1) of the product gas, so that the number of steps and the size and cost of recovery equipment, are greatly reduced. The tail gas consists mainly of pure hydrogen. If this is not needed for other syntheses, it can be used as fuel for heating the furnace. About 80 – 87 % of the ammonia and 90 – 94 % of the methane are converted to hydrogen cyanide. The specific energy consumption of ca. 4 × 10<sup>6</sup> kJ/100 kg HCN reported thus far has been considerably decreased by more recent developments [70, 71]. A large part of the heating energy is recovered and used in the air preheater or steam generator.

If the methane supply is limited, the process can be carried out directly with liquefied hydrocarbons or ethanol, or in a three-step reaction starting from methanol [72–74]. Both Degussa and Lonza utilize the BMA route to produce hydrogen cyanide.

### 1.2.3. Shawinigan Process

In the Shawinigan process, hydrocarbon gases are reacted with ammonia in an electrically heated, fluidized bed of coke. The process, sometimes called the Fluohmic process, was developed in 1960 by Shawinigan Chemicals [75–78], now a division of Gulf Oil Canada.

In a circular reaction cavity constructed from alumina and silicon carbide, the mixture of ammonia and hydrocarbon (N/C ratio slightly > 1) passes through a fluidized bed of coke, heated by electrodes immersed in the bed. The chemical reaction is similar to the methane – ammonia process, but no catalyst is required and temperatures are kept above 1500 °C. Other carbon compounds, such as naphtha or lighter hydrocarbons, can also be converted. Propane is usually the main feedstock. The reaction can be described as



Unreacted feed gas is almost completely decomposed to the elements. This reduces the quantity of ammonia to be removed from the product gas and leads to the formation of coke particles. The control of coke particle size in the bed is an important operating parameter.

The reactor effluent contains up to 25 vol % HCN, 72 vol % H<sub>2</sub>, 3 vol % N<sub>2</sub>, and only 0.005 vol % NH<sub>3</sub>. Coke is removed in a water-cooled, cyclone-entrained bed. The gas is further cooled and enters the absorption equipment where HCN is removed. The residual gas, nearly pure hydrogen, can be used for other chemical processes. Some of the hydrogen is recycled to the reaction unit to inhibit the formation of soot.

Coke from the cyclone is screened, and three fractions are separated, stored, and then fed back to the reactor system in the desired proportions to control the particle size distribution. By regulating the rate of coke recycling, the level of the fluidized bed and the reaction temperature can be controlled.

In practice, at least 85 % of the ammonia and up to 94 % of the hydrocarbon are converted to hydrogen cyanide. Because of the high electric power consumption (6.5 kWh per kilogram of HCN) the Shawinigan process would probably only be attractive where low-cost electricity is available.

This process is employed by Polifin in South Africa, by Arogenesas in Spain, and by Ticor in Australia.

### 1.3. Storage and Transportation [79, 80]

Handling, storage, and transportation of hydrogen cyanide are determined by its low boiling point, high toxicity, and instability in the presence of moisture, bases, or other impurities. The liquid acid is relatively uncorrosive. Materials compatible with HCN at normal temperatures are stainless steel, Hastelloy, and Monel. To prevent polymerization, stabilizing agents, such as sulfuric acid, phosphoric acid, oxalic or acetic acid, and sulfur dioxide are used. The type and quantity of stabilizer (usually < 0.5 %) depend on storage capacity, temperature, and residence time in a container. A combination of H<sub>2</sub>SO<sub>4</sub> and SO<sub>2</sub> prevents the decomposition of HCN in the liquid and vapor phases. Larger quantities of hydrogen cyanide are stored at a maximum temperature of 5 °C and must be permanently recirculated.

Additionally, the color of the liquid is monitored and should not exceed APHA 20. To keep the concentration of gas below the danger level, good ventilation of buildings in which HCN is stored and handled is of primary importance. Hydrogen cyanide is usually classified by governmental authorities as very poisonous, requiring special packaging and transportation regulations. Similar strict procedures exist for solutions with an HCN content of 5 % or more. Smaller quantities of the stabilized acid are transported in metal cylinders of up to 56 kg nominal water capacity in the United States and up to 60 kg in Germany. Cylinders cannot be charged with more than 0.55 – 0.60 kg of liquid HCN per 1 L bottle, and resistance to deformation must be tested up to 10 MPa before first filling. The water content should not exceed 3 %, and storage time should be less than one year. According to national regulations, transportation of quantities > 100 kg requires special permission. Procedures covering details of tank car size (up to 50 t), shipping, loading, and handling must be obeyed.

Hydrogen cyanide is mainly shipped by rail under the provisions of the applicable transport regulations. Transport in railcars is permitted

only by approval of the competent authorities. The transport classifications of the most common transport regulations are as follows:

RID/ADR: Class 6.1, 1°; (a).

CFR 49: Class 6.1, UN 1051, PG I, "Poison Inhalation Hazard, Hazard Zone A".

#### 1.4. Economic Aspects and Uses

In 1998 the production capacity of synthetic hydrogen cyanide was about  $650 \times 10^3$  t/a in the United States,  $400 \times 10^3$  t/a in Europe, and  $35 \times 10^3$  t/a in Japan. Without detailed knowledge of the type and age of catalyst used in various acrylonitrile plants, the additional amount of byproduct HCN can only be estimated. With an estimated HCN formation in the acrylonitrile processes of 10 %, an additional  $180 \times 10^3$  t/a (United States),  $130 \times 10^3$  t/a (Europe), and  $60 \times 10^3$  t/a (Japan) is available. Currently, between 60 and 80 % of the existing production capacity is being utilized. The variety of uses has changed enormously in the past 15 years. Acrylonitrile production starting from acetylene was formerly the major consumer of hydrogen cyanide; in contrast, the Sohio process now in use yields HCN as a byproduct.

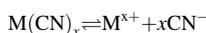
Today, the main outlet for HCN is the manufacture of methyl methacrylate. Acetone is treated with hydrogen cyanide to produce acetone cyanohydrin, which is treated with sulfuric acid and methanol to form methyl methacrylate. HCN is used to a similar extent in adiponitrile production, in which 2 mol HCN are added to 1 mol butadiene in a two-stage process. Virtually all the adiponitrile is then converted to hexamethylenediamine, a nylon precursor. Hydrogen cyanide reacts with chlorine to form cyanogen chloride (see Section 4.2) which is usually directly trimerized to cyanuric chloride. Herbicides based on cyanuric chloride have been successfully employed in recent years.

D,L-Methionine, one of the largest volume amino acids produced commercially, is manufactured in a complex, multistep synthesis which employs hydrogen cyanide as one of the raw materials. Other uses of HCN are in the production of chelating agents such as ethylenediaminetetraacetic acid (EDTA) or nitrilotriacetic acid (NTA), starting from aldehydes, amines, and hydrogen cyanide. A wide variety of organic

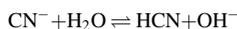
intermediates can also be made from HCN and have considerable potential utility. The most important derivatives of hydrogen cyanide in inorganic chemistry are alkali metal cyanides and cyanide complexes of iron.

## 2. Metal Cyanides

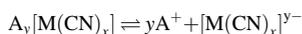
Metal cyanides are compounds of metals in which one or more cyanide ions act as monodentate ligands with carbon as the preferred donor atom. Simple metal cyanides are represented by the formula  $M(CN)_x$ . Depending on the metal, simple cyanides dissolve more or less readily in water, forming metal ions and cyanide ions:



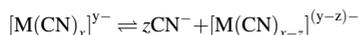
The solubility is influenced by pH and temperature, especially because hydrogen cyanide is formed by the hydrolysis of cyanide:



The cyanide complexes can generally be described by the formula  $A_y[M(CN)_x]$ , where A is an alkali, alkaline earth, or heavy metal, and M is normally a transition metal. Most cyanide complexes in which A is an alkali or alkaline earth metal are highly soluble in water and form alkali or alkaline earth metal ions and complex transition metal cyanide anions, e.g.,



The complex cyanide anion may then undergo further dissociation and release cyanide ions:



The dissociation of the cyanide complex depends strongly on the type and valency of the complexed metal ion, as well as on the pH and concentration of the solution. Insoluble or slightly soluble cyanide complexes are formed when the alkali or alkaline earth metal anion A is replaced by a heavy metal ion. In this case, more complicated cyanide complexes are often formed, which cannot be described by the above-mentioned formula. Furthermore, most heavy metal ions allow the formation of mixed cyanide complexes in which one or more of the cyanide groups can be replaced by other ligands

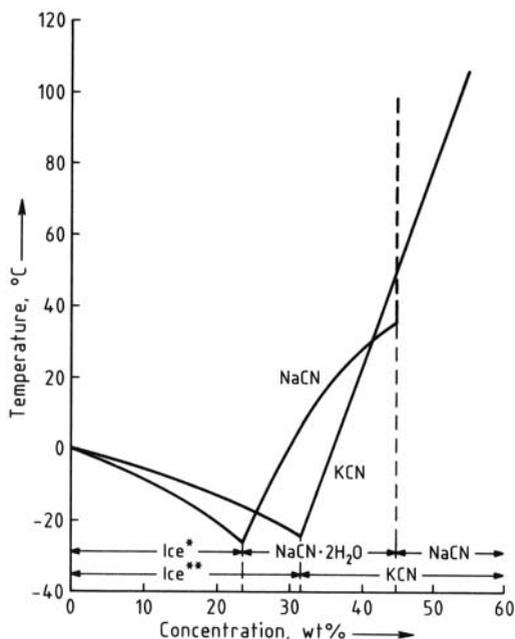
such as halides, pseudohalides, nitrogen oxides, sulfur compounds, water, or ammonia [4]. The properties and toxicities of these compounds depend on the structures of the metal cyanides.

## 2.1. Alkali Metal Cyanides

Since the introduction of the Castner process, sodium cyanide [143-33-9] has been the metal cyanide with the greatest commercial importance. Until about 1900, potassium cyanide [151-50-8] was the more common compound, because it could be produced more easily by melting potassium carbonate with potassium hexacyanoferrate(II), one of the oldest known cyano compounds. The properties and reactions of both alkali cyanides are very similar.

### 2.1.1. Properties

Sodium and potassium cyanide are colorless, hygroscopic salts with a slight odor of hydrogen cyanide and ammonia in moist air. They are fairly soluble in water (Fig. 4), and the sodium salt forms two hydrates:  $\text{NaCN} \cdot 2 \text{H}_2\text{O}$  below  $35^\circ\text{C}$  and  $\text{NaCN} \cdot 1/2 \text{H}_2\text{O}$  at higher tempera-



**Figure 4.** Solubility of NaCN and KCN in water

\* Solid phase: ice- $\text{NaCN} \cdot 2 \text{H}_2\text{O}$  or ice- $\text{NaCN}$

\*\* Solid phase: ice-KCN

tures. Further physical properties are listed in Table 2. In the absence of air, carbon dioxide, and moisture, the alkali metal cyanides are

**Table 2.** Physical properties of NaCN [143-33-9] and KCN [151-50-8]

Physical quantity	NaCN	KCN
$M_r$	49.015	65.119
$mp$	$561.7^\circ\text{C}$ (98 wt %)	$634.5^\circ\text{C}$
$bp$	$1500 \pm 10^\circ\text{C}$	
q, density	1.620 $\text{g}/\text{cm}^3$ ( $6^\circ\text{C}$ , rhombic) 1.595 $\text{g}/\text{cm}^3$ ( $20^\circ\text{C}$ , cubic) 1.19 $\text{g}/\text{cm}^3$ ( $850^\circ\text{C}$ , fused)	1.553 $\text{g}/\text{cm}^3$ ( $20^\circ\text{C}$ , cubic) 1.56 $\text{g}/\text{cm}^3$ ( $25^\circ\text{C}$ , cubic)
$c_p$ , specific heat capacity	1.667 $\text{kJ kg}^{-1} \text{K}^{-1}$ ( $273.1 \text{ K}$ ) 17.950 $\text{kJ kg}^{-1} \text{K}^{-1}$ ( $288.0 \text{ K}$ ) 1.402 $\text{kJ kg}^{-1} \text{K}^{-1}$ ( $298.6 \text{ K}$ )	1.00 $\text{kJ kg}^{-1} \text{K}^{-1}$ ( $25 - 72^\circ\text{C}$ )
$H_f$ , enthalpy ( $25^\circ\text{C}$ )	$-89.9 \text{ kJ/mol}$	$-112.63 \text{ kJ/mol}$
$\Delta H_f$ , heat of fusion	314 $\text{kJ/kg}$	225 $\text{kJ/kg}$
$\Delta H_v$ , heat of vaporization	3185 $\text{kJ/kg}$	
$p_v$ , vapor pressure	0.10 $\text{kPa}$ ( $800^\circ\text{C}$ ) 1.65 $\text{kPa}$ ( $1000^\circ\text{C}$ ) 11.98 $\text{kPa}$ ( $1200^\circ\text{C}$ ) 39.10 $\text{kPa}$ ( $1350^\circ\text{C}$ )	
Solubility in 100 g of		
Water	see Figure 4	see Figure 4
Ethanol, 100 %	1.235 g ( $25^\circ\text{C}$ )	0.57 g ( $19.5^\circ\text{C}$ )
Ethanol, 95 %	2.445 g ( $25^\circ\text{C}$ )	
Methanol	6.44 g ( $15^\circ\text{C}$ ) 4.58 g ( $25^\circ\text{C}$ ) 4.10 g ( $67.4^\circ\text{C}$ )	4.91 g ( $19.5^\circ\text{C}$ )
$\text{NH}_3$ , liquid	58 g ( $-31^\circ\text{C}$ )	4.55 g ( $-33.9^\circ\text{C}$ )

stable, even at fairly high temperature, and can be stored indefinitely [2].

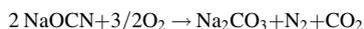
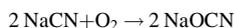
Dry CO<sub>2</sub> does not react with dry alkali metal cyanides; however, in moist air slow decomposition takes place, even at normal temperature, releasing HCN:



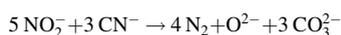
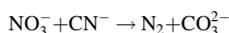
When this occurs, the salt sometimes becomes brownish because of the formation of polymerization products of HCN (azulmic acid). Alkali metal cyanides are totally decomposed to HCN by the action of strong acids, e.g.,



At elevated temperatures, oxygen reacts with alkali metal cyanides, to form the metal cyanate and carbonate, nitrogen, and carbon dioxide [83]:

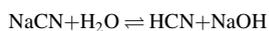


The oxidation of alkali metal cyanides to cyanates by bubbling an air stream through an alkaline melt is used for the bath nitriding of steel [84, 85]. Oxides of lead, tin, copper, nickel, and iron react with alkali metal cyanides above 560 °C to form the corresponding cyanate and carbonate, nitrogen, carbon dioxide, and the corresponding metal [86, 87]. Violent oxidation of alkali metal cyanides can result from the addition of strong oxidants such as nitrate, nitrite, or chlorate to a melt:



These reactions have been utilized for the destruction of waste salts from hardening shops [88, 89].

When alkali metal cyanides are dissolved in water, a pH-dependent, reversible equilibrium is established between hydrocyanic acid and alkali-metal hydroxide [90, 91]:



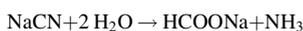
For example, in an aqueous solution of NaCN at pH 9.4, half of the total cyanide is present as HCN [92] (cf. Fig. 1). As a result of this hydrolysis, solutions of alkali-metal cyanides in water are always strongly alkaline. Furthermore, com-

**Table 3.** pH values of aqueous solutions with varying concentrations of NaCN and KCN [76]

	Concentration, mol/L					
	1	10 <sup>-1</sup>	10 <sup>-2</sup>	10 <sup>-3</sup>	10 <sup>-4</sup>	10 <sup>-5</sup>
NaCN	11.64	11.15	10.67	10.15	9.6	8.9
KCN		11.37	10.91	10.35		

mercial products always contain small amounts of alkali metal hydroxide to enhance stability; hence, the actual pH values of solutions are usually higher than those calculated on the basis of the cyanide concentration and the hydrolysis reaction (Table 3).

Nevertheless, when alkali metal cyanides are dissolved in tap water, discoloration and precipitation of brownish-black amorphous polymerization products of HCN (azulmic acid) may occur when the water contains too much CO<sub>2</sub> or other acidic components. When solutions of alkali-metal cyanides are stored for a long time or heated, slow hydrolysis of the C≡N bond takes place to yield the alkali metal formate and ammonia [93, 94]:



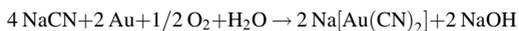
The hydrolytic decomposition of concentrated NaCN solutions can be suppressed, even at 60 – 80 °C, by the addition of 0.5 – 2 % NaOH [95]. However, the hydrolysis is fast and complete when the reaction is carried out at 170 °C under pressure [96, 97]. This process has been investigated for the destruction of cyanide wastes from metal hardening plants [98]. Atmospheric oxygen achieves only partial oxidation of cyanide in aqueous solution at elevated temperature [99]; however, the reaction can be enhanced by the use of catalysts such as activated carbon [100, 101]. A fast conversion of cyanide to cyanate is brought about by ozone at pH 10 – 12; this is followed by a slower oxidation to nitrogen and carbonate [102, 103].

Cyanide is also oxidized to cyanate by hydrogen peroxide [104] and by peroxomonosulfate, peroxodisulfate [105], and permanganate ions [106]. The anodic oxidation of cyanide leads, via cyanogen and the cyanate, to the carbonate, nitrogen, ammonia, and urea [107]. Halogens react with cyanide in aqueous solution to give cyanogen halides, XCN (X = Cl, Br, I), which are hydrolyzed more or less quickly, depending

on the pH and temperature of the solution [108] (see Section 4.1).

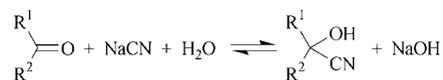
Reaction with chlorine or hypochlorite above pH 11.5 is the most widely used process for detoxification of solutions and wastewaters containing cyanide at concentrations below 1 g/L.

The reaction of alkali cyanides with sulfur or polysulfides in aqueous solution at elevated temperature is used for the production of alkali metal thiocyanates [109]. The reaction with thiosulfate to give thiocyanate is used therapeutically in the treatment of cyanide poisoning [110]. Heavy metal ions react in aqueous solution with cyanide to yield insoluble cyanides, all of which dissolve in the presence of excess cyanide to give stable complex salts [111]. These compounds play an important role in metallurgy and electroplating [112]. Some base metals (e.g., zinc or nickel) and, in the presence of oxygen or oxidizing agents, even precious metals (e.g., gold or silver) are dissolved by aqueous solutions of alkali metal cyanides [113]. This property of alkali metal cyanides has been utilized for about 100 years in the leaching of precious metals ores:

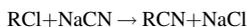


Tantalum, titanium, and tungsten are not attacked by alkali metal cyanide solutions at room temperature.

Alkali metal cyanides react with carbonyl groups of organic compounds in aqueous solution to form cyanohydrins [115, 116]:



Organic compounds with labile halogen atoms can be converted by reaction with alkali metal cyanides in aqueous solution to nitriles, which can be further processed to give carboxylic acids, amines, etc.:



## 2.1.2. Production

Sodium and potassium cyanide are produced by reaction of: gaseous or liquid HCN reacts with a

solution of sodium or potassium hydroxide. The formation of cyanides is chemically a simple neutralization reaction between a weak acid (HCN) and a strong base (OH<sup>-</sup>). The neutralization reaction has an energy release of 460 kJ/mol, which leads to additional heating of the reaction solution and saves energy.

The efficiency of the neutralization reaction is very high, and the yield based on HCN is close to 100 %. Thus all of the HCN used is transferred into the end products NaCN or KCN, and only minimal losses of HCN occur.

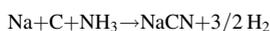
The reaction results in the formation of a dissolved salt. The raw solution can either be concentrated or diluted with water, depending on what kind of intermediate product form is produced. Normally, the aim is to form a concentrated solution with ca. 30 % cyanide. Commercial solid sodium and potassium cyanide can be crystallized by evaporation of excess water.

There are patented cyanide production processes available which directly form solid material in a fluidized-bed reactor using an alkali solution and HCN gas as raw materials. Also processes are patented that use a cyanide solution as the cyanide source, and solid cyanide is produced by a drying process in a fluidized-bed reactor.

### 2.1.2.1. Classical Production Processes

The following processes are termed classical as they are not applied to any significant extent in Europe presently but were used in earlier cyanide production.

In the *Castner – Keller process* sodium metal reacts with charcoal and ammonia at around 600 °C in a melt [117]:



This process was mainly developed by Degussa and applied there until 1971.

The *calcium cyanamide process* is very similar to the Castner process, but uses calcium carbonate as the carbon source for the cyanide ion.

In the “*blood process*” potassium or sodium carbonate was fused with potassium hexacyanoferrate(II), for which mainly animal blood and wastes were used as raw materials.

### 2.1.2.2. Current Production Processes

Cyanides are made by melt processes or by processes in aqueous solution using HCN as the cyanide source. Most cyanide is produced nowadays using solution processes. Only where (electrical) energy costs are sufficiently low can melt processes be competitive.

Melt processes do not apply any cyanide sources as raw materials, but produce the cyanides from non-cyanide components. The result of the processes is a solid cyanide with different kinds of impurities, e.g., carbon black from using carbon as raw material.

Cyanides can be produced in batch and in continuous operation. Liquid cyanide solutions are easily pumped as the viscosity is moderate even at the highest achievable concentration.

Figure 5 shows a flow sheet for NaCN production.

**Production of Cyanide Solution.** The production of the cyanide solution (NaCN, KCN) is the basic first production step. Further processing of the resulting raw cyanide solution usually consists of concentration of the solution by



Figure 5. Example of a solid cyanide production plant

evaporation of excess water, cooling, filtering, and storage. The exact ratios of cyanide in water are strongly dependent on the water balance. When a concentrated NaOH solution (50 %) and pure HCN (99 %) are used a cyanide solution with ca. 46 % sodium cyanide is formed which needs to be further diluted with water to give a commercial product.

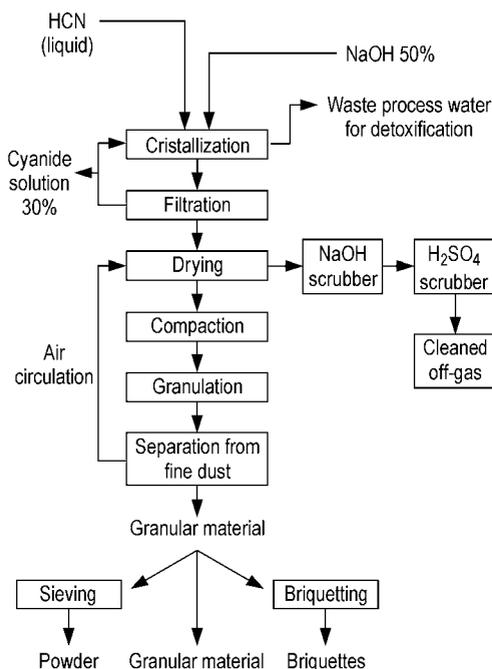
Solutions are often directly used in cases where the site of industrial application is close enough to the cyanide production site to keep the transport of solution competitive (energy for evaporation of the excess water, formulation of the solid material). This is, therefore, usually only applied if the application site can directly use a concentrated cyanide solution (30 wt %). This is, for example, the case for gold mining operations in Nevada, South Africa, and Australia. Cyanide solution is normally shipped in tank trucks to the gold mine, subsequently stored in liquid tanks at the site, and diluted for further use, if necessary.

Many gold mines are too far away from the raw material production site to be supplied with liquid material and, therefore, need solid NaCN.

Cyanide solutions normally contain approx. 24 – 30 % NaCN. Cyanide solutions transported at cold times of the year or in cold regions may contain lower cyanide concentrations to prevent crystallization during transport and storage in unheated devices.

In cases where an application requires HCN as a liquid or a gas and no HCN production is available on site, cyanide solutions or solids can be used as the source. They need only be acidified, and the HCN is distilled and taken to production. Normally, it is not stored intermediately.

**Production of Solid Cyanides.** Solid cyanide is made from solution by crystallization of solid cyanides from the liquid, separation of the wet solid with further drying and mechanical handling to form stable solid product forms. Figure 6 shows a plant for the production of solid cyanides. The preferred solid forms are bricks, granules, tablets, and powder. Bricks are made by compacting of the wet filter cake with subsequent drying and also by first drying the crystals followed by compacting. Bricks are also made from granules. Powder can be made by



**Figure 6.** Flow chart of the main production steps for cyanide production (NaCN as example)

grinding and subsequent sieving of fines material.

The cyanide content in solids is usually very high and specified for normal applications in a range of higher than 98 % and even higher than 99 %.

### 2.1.2.3. Energy Consumption

The energy costs for cyanide production are mainly due to electricity and steam and correspond to approx. 1.3 – 1.5 t of steam per ton of solid 100 % NaCN or KCN.

### 2.1.3. Packaging and Transport [118, 119]

Production includes packaging of cyanides for the safe storage and transport. Normally cyanides are filled into metal drums holding between 50 and 100 kg or 1 t big bags which are transported in wooden boxes. All packaging must have UN registration for the packaging of hazardous materials. Returnable packaging for multiple use is an important alternative to the use of one-way



**Figure 7.** Storage facility for solid cyanide in drums

packaging. Both one-way packaging and returnable packaging for solid material are used worldwide. Another alternative for transport is the so-called solid to liquid system (SLS). Here, solid cyanides are filled into a unit containing approx. 20 t of material. This unit is transported to the customer's site and the cyanide is dissolved directly at the user's facility and pumped to a storage tank. The transportation unit can be reused and refilled with solid material many times. The preferred type of packaging often depends on the specific transport conditions, which are due to technical, economical, and environmental considerations.

Figure 7 shows storage of solid cyanide in drums.

Transport is regulated by national and international regulations and laws:

RID/ADR and ADNR	Class 6.1
UN no	1680 (KCN)
	1689 (NaCN)

Road transport of liquid cyanides is allowed in various European countries. However liquid cyanide is preferably shipped by rail cars within Europe. Only certified companies with a special permit for the transportation of dangerous goods are approved. Some European countries require special permits for the transport of cyanides on the road, e.g., Italy. Each transport in Europe is also required to have a transport emergency card with relevant information on cyanide on board.

In Germany, it is allowed to ship cyanides and acids together in the same shipment (trucks). But for safety reasons cyanides and acids should not be transported and stored together.

Transportation of cyanide solution is mostly favored in cases where transport routes to the end-users are considered to be safe and the distance short enough that transport of liquid products is economic compared to the alternative of solid cyanide. Also the customer must be in the position to directly use the solution.

Production of solid material from cyanide solutions is mostly the best alternative when the product is transported over long distances, when the transport of liquid is not allowed according to national regulations, and when the customers are prepared to store and use solid material.

#### **2.1.4. Responsible Care, Product Stewardship, Sustainable Development, Certification** [120–132]

Production facilities can be certified according to international standards referring to product and management system quality including the relevant aspects of (workers') health, safety, and environmental management or any other systems that lead to similar results. This includes certification according to ISO 9001, 14001, or any other management system that is applicable to manage company and stakeholder needs sufficiently.

Cyanide producers who supply cyanide to gold mines are increasingly being asked to fulfill the requirements of the cyanide producers verification audit protocol according to the International Cyanide Management Code (ICMC) provisions. The overall basis for this kind of certification is the International Cyanide Management Code for the gold mining industry.

All cyanide producers supply material safety data sheets (MSDS) to their customers covering all specific information needed for the safe handling and use of their products. Information and training programmes are in place for traders, end-users, and transport companies.

Transport route analysis from the production facility to the sites of the end-users (mainly for the mining industry) are carried out by producers.

Major European cyanide producers exchange information on safety, health, and environmental aspects of their products on a regular basis within the CEFIC Cyanide Sector Group. This group

has, for example, developed a Mutual Aid Scheme (MAS) for transportation incidents with cyanides and published the "Guidelines for Storage, Handling, and Distribution of Alkali Cyanides".

#### **2.1.5. Emissions and Consumptions** [133–139]

**Hazardous Emissions** from cyanide production can be emissions of HCN and NH<sub>3</sub> gases and of cyanides, the last-named mainly in wastewater or as particles in the workplace.

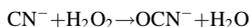
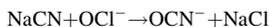
NH<sub>3</sub> and HCN can be detected by humans due to their specific odor at low detection limits. These limits are far below any workplace limits. Therefore, people may be warned even without any technical monitoring devices. However, a significant number of persons are not able to detect HCN, and a much smaller number can not detect NH<sub>3</sub> by its smell. Hence, in accordance with standard workplace regulations, monitoring devices must be installed, mainly for the detection of HCN and also for NH<sub>3</sub>.

The production of cyanide solutions is operated under closed conditions where no HCN can leak from the units. As a result the overall emission of HCN from cyanide production plants in Europe and elsewhere are below the European and national regulation limits (e.g., TA Luft in Germany) and below 10 kg HCN per year for a 20 000 t/a production facility.

NH<sub>3</sub> emissions may result from heating cyanides and cyanide solutions. NH<sub>3</sub> formation from cyanide production can result from the hydrolysis of cyanides at higher temperature, which can result in the formation of cyanate. The formation and the subsequent emission of NH<sub>3</sub> to the environment is very low and below reportable limits, i.e., less than 15 kg NH<sub>3</sub> per year.

**Detoxification of Cyanides.** The detoxification of cyanides can be carried out by using different kinds of oxidizing agents, such as hypochlorite or peroxides. Pure oxygen is not suitable. Using hypochlorite creates a significant salt load of the effluent and can create additional contributions to AOX load. Using H<sub>2</sub>O<sub>2</sub> based technology does not create any of

these byproducts and can be seen as the best choice for cyanide detoxification at a cyanide production plant.



Cyanide which is dissolved in process wastewater can be treated by the above-mentioned methods, but preferably peroxides are used.

**Wastewater.** The process solution can directly be fed to a biological treatment plant under predefined conditions. Also diluted cyanide effluent streams may directly be added to a biological wastewater treatment, where bacteria break down the cyanide to nontoxic substances and use the chemical as feed.

As a result of detoxification the free cyanide in the treated water is far below 0.01 ppm. The total amount of cyanide transferred to the environment from a 20 000 t/a NaCN plant normally is below 50 kg/a. These small cyanide emissions which enter, e.g., rivers at a very low concentration do not pose harm to fish and the environment and are much likely also detoxified further by microorganisms.

Excess water from concentrating cyanide solutions is evaporated and either recycled to the process water after condensation or detoxified as mentioned above. No contaminated water is emitted to the air.

While most of the evaporated water is subsequently condensed, a small amount of the vapors and noncondensables must be treated before release to the atmosphere. This is accomplished through the use of wet scrubbers, incineration, or a combination of both. Wet scrubber systems utilize liquid scrubbing solutions designed to contain or neutralize the noncondensable gases. Destruction efficiencies for these systems exceed 98 %. Incineration or thermal oxidation systems are also utilized for detoxification of the gasses. Destruction efficiencies for these systems exceed 99 %.

### 2.1.6. Quality Specifications, Impurities

The main impurities arising during the production of cyanides are cyanate ( $\text{OCN}^-$ ), formate

( $\text{HCOO}^-$ ), and carbonate ( $\text{CO}_3^{2-}$ ). However, generally speaking, none of these are critical in any way for the applications in gold mining, the chemical industry, and electroplating. Very often these impurities are formed in application processes anyway.

Carbonates originate mainly from contact of excess alkali in the cyanide solution with atmospheric carbon dioxide. Hydrolysis of cyanide at higher temperatures (e.g., in drying sections, in hot solutions) leads to an increased content of formate, and ammonia is also formed. Cyanate can be formed by oxidation.

Ammonia can also occur as a possible impurity, especially in solutions after longer storage at elevated temperatures. If slow hydrolysis in solid (wet) material takes place, the ammonia formed can be released to the gas phase.

Due to reactions that lead to the formation of HCN and/or  $\text{NH}_3$  commercial cyanide solutions can – mainly after prolonged storage under non-ideal conditions – have a smell of HCN and/or  $\text{NH}_3$ . Absolutely dry cyanides normally do not smell of these species, as the presence of water is necessary for any of the decomposition reactions that lead to the release of HCN and/or  $\text{NH}_3$ .

For high-quality applications in the electroplating industry the content of a number of heavy metals is critical. Therefore, these must be below specified limits, which are, for example, defined in the DIN-ISO 50971. To achieve the DIN standards the respective alkali metal source (NaOH, KOH) must meet these requirements, as only these raw materials can act as sources of these metals. Due to its production processes, HCN is free of these metals.

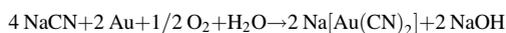
For applications in high-quality electroplating and for most chemical synthesis applications, especially for the pharmaceutical industry, the specification for cyanides according to DIN-ISO 50971 can be regarded as a typical minimum quality requirement (Table 4).

### 2.1.7. Uses

#### 2.1.7.1. Gold Mining [140–145]

The majority of world sodium cyanide production is used in gold mining to extract gold from its ores ( $\rightarrow$  Gold, Gold Alloys and Gold Compounds, Section 4.2). Elemental gold is very stable and

does not react easily, even with very aggressive chemicals. Usually only in the presence of a strong oxidant together with a complexing agent can gold become water-soluble (formation of soluble gold salts). A classical example of how gold can be dissolved is the use of aqua regia, a mixture of the strong oxidant  $\text{HNO}_3$  and the complexing agent  $\text{HCl}$ , where the chloride ion is the complexant for the gold. More weakly oxidizing conditions can be applied if a very strong complexing anion is used. In gold mining, cyanide is the complexing agent for the gold. Even by oxidation with oxygen (air, peroxides) under normal reaction conditions (dilute, slow reaction speed, moderate to low temperature) elemental gold is dissolved by oxidation and then subsequently complexed with cyanide:



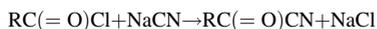
While the gold chloride complex is unstable in dilute aqueous solution, even very low concentrations of the gold cyanide complex are stable in water over a wide pH range.

Cyanides are used in gold mining, although they are acutely toxic, mainly because of their high efficiency and selectivity, and they can not easily be substituted by other chemicals. In gold mining, not using cyanides would basically mean the termination of primary gold production. Only approx. 10 % of gold production today runs without the application of cyanides. There have been numerous attempts to develop gold mining processes using alternative lixivants for gold extraction. None of the alternative lixivants or processes have ever been applied successfully in any large-scale operation on a worldwide basis. In this sense, only cyanide can fulfil the requirements of the gold mining industry to extract gold from the variety of ores in an economical and environmentally sound manner.

### 2.1.7.2. Chemical Synthesis

In a number of reactions, cyanides are used as starting materials or intermediates. In organic chemistry the cyano group basically acts as a building block which can easily be transformed into a variety of other chemical functional groups, such as carboxylic acids, esters, hydroxylamines, cyanohydrins, and many more. Important examples in chemical synthesis are

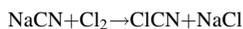
the cyanidation of acyl chlorides forming acyl cyanides as intermediate products:



and the nucleophilic substitution of halogenated alkanes by alkali metal cyanides for the elongation of the molecular chain by one carbon atom:



Another basic reaction is the formation of cyanogen chloride from sodium cyanide and chlorine:

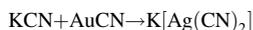
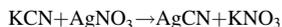


Trimerization of cyanogen chloride results in the formation of cyanuric chloride ( $\rightarrow$  Cyanuric Acid and Cyanuric Chloride, Chapter 3), an important raw material for the production of herbicides, pesticides, fungicides, and insecticides. Cyanides are therefore important raw materials for crop-protection agents in the worldwide agricultural market.

### 2.1.7.3. Electroplating of Metals

( $\rightarrow$  Electrochemical and Chemical Deposition)

The electroplating industry uses silver and gold cyanides for electroplating processes:



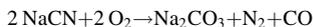
Beside the similar gold cyanide and potassium dicyanoaurate(I) the trivalent gold cyanide compound  $\text{K}[\text{Au}(\text{CN})_4]$  has the advantage of working in lower pH ranges and is able to deposit gold directly onto stainless steel base materials.

Electroplating of platinum metals is performed in cyanide baths and, for special applications, in cyanide melts. The high-temperature electroplating (HTE process) runs in the temperature range of 500 – 600 °C in an eutectic sodium – potassium cyanide mixture under argon gas.

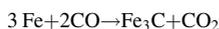
### 2.1.7.4. Hardening of Metals

Strongly treated steel, such as that camshafts for motors, must be hardened by boron, nitrogen, or carbon. One of the most favorably applied methods is the carbonization of the metals in melts with cyanide. A superficial layer of iron

carbide, Fe<sub>3</sub>C (martensite) with a depth of several micrometers is formed at a temperature of about 900 °C. By the addition of barium chloride as activator the amount of cyanide could be minimized to some extent. The main chemical reactions of the hardening process are:



and



and hence the overall reaction:



The regeneration of such melts is possible with nonhazardous polymeric cyanic acid, azulminic acid [CNH]<sub>x</sub>, cyanamide NH<sub>2</sub>CN, dicyanamide, or melamine under nitrogen atmosphere.

### 2.1.8. Economic Aspects

The most important alkali metal cyanides in terms of production volume are sodium cyanide and potassium cyanide. Potassium cyanide production worldwide amounts to less than 10 % of the sodium cyanide production. The same production facilities can be used for the manufacture of NaCN and KCN.

In Europe, NaCN and KCN are produced at less than ten sites for various purposes. A significant amount is produced for captive use, but the majority is produced for applications within Europe and for export outside Europe.

Cyanide production efficiency is mainly driven by cost-effective production conditions. The production costs are mainly influenced by the costs for the raw materials HCN and NaOH/KOH, which can differ significantly.

In the 1990s the cyanide producer market in Europe consolidated to a significant extent, and a number of production sites have been closed. Existing production sites in Europe as of 2005 follow (asterisk denotes captive use):

Wesseling, Germany	NaCN solution, NaCN solid, KCN solid
Geleen, the Netherlands	NaCN solution
Billingham, United Kingdom	NaCN solution
Ludwigshafen, Germany	NaCN solution
Antwerp, Belgium	NaCN solution
Kolin, Czech Republic	NaCN solid

Pitesti, Rumania	NaCN solution
Seal Sands, United Kingdom*	NaCN solution
Saint-Avold, France*	NaCN solution
Roussillon, France*	NaCN solution

The production capacity of cyanides in Europe is in the range of 90 000 t/a (based on 100 % solid material). Most of this is solid sodium cyanide; a smaller part is solid potassium cyanide. Worldwide sodium cyanide production is estimated at approx. 500 000 t/a.

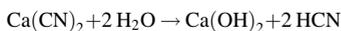
About 70 % of world cyanide production is used in the gold mining industry. The second biggest application is in industrial chemical synthesis, and third is electroplating together with metal hardening.

In Europe the majority of cyanide production is used in chemical synthesis. The second largest application is electroplating together with metal hardening, and the third is the mining industry.

The differences in prices between NaCN and KCN are mainly reflected in the price differences of the raw materials NaOH and KOH. As KOH is significantly higher in price, KCN is also more expensive than NaCN. Selling prices in Europe for NaCN/KCN are also subject to fluctuation on the world market. Prices were mainly less than 1650 \$/t for NaCN (100 %) and less than 3000 \$/t for KCN (100 %).

## 2.2. Alkaline Earth Metal Cyanides

**Properties and Uses.** The properties of the alkaline earth metal cyanides differ from those of the alkali metal cyanides. They are less stable and decompose at elevated temperatures to release HCN. Even when alkaline earth metal cyanides are in contact with moist air or dissolved in water, hydrolysis takes place, e.g.,



As a consequence, pure solid calcium cyanide is unstable, and the commercial product can only be manufactured in amorphous form with a content of about 45 – 50 % NaCN equivalent, known as black cyanide. As a solution, calcium cyanide is only sufficiently stable for commercial use at concentrations below 17 %.

Liquid and solid calcium cyanide are only produced in South Africa, where they are used

**Table 4.** Specifications and average analysis of NaCN and KCN (data given in wt % or ppm = mg/kg; M = Na or K)

	NaCN		KCN	
	DIN 50 971	Average analysis	DIN 50 971	Average analysis
MCN, %		> 98.0	98 – 99	
CN <sup>-</sup> , %	51.5	> 52.0	39.0	> 39.0
MOH, %		≈ 0.5		≈ 0.1
M <sub>2</sub> CO <sub>3</sub> , %		≈ 0.5		≈ 1.0
Cl <sup>-</sup> , %		≈ 0.02		≈ 0.0015
SO <sub>4</sub> <sup>2-</sup> , %		≈ 0.05		< 0.01
SO <sub>3</sub> <sup>2-</sup> , %		< 0.05		< 0.01
S <sup>2-</sup> , ppm		< 1		< 1
MOCN, %		≈ 0.1		≈ 0.1
SCN <sup>-</sup> , %		< 0.01		< 0.01
HCOOM, %		≈ 0.5		≈ 0.3
H <sub>2</sub> O, %		≈ 0.2		≈ 0.2
Sb, ppm	< 5	< 5	< 5	< 5
As, ppm	< 5	< 5	< 5	< 5
Pb, ppm	< 50	< 50	< 50	< 50
Cd, ppm	< 10	< 10	< 10	< 10
Fe, ppm	< 50	< 50	< 50	< 50
Cu, ppm	< 10	< 10	< 10	< 10
Ni, ppm	< 50	< 50	< 50	< 50
Zn, ppm	< 20	< 20	< 20	< 20
Sn, ppm	< 80	< 80	< 30	< 30
Na, %		< 48	< 0.5	< 0.3
Insolubles, %	< 0.005	< 0.001	< 0.005	< 0.001

for the leaching of precious metals from ores [148].

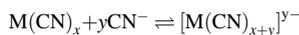
Apart from this compound, only barium cyanide has any commercial importance as a result of its use in electroplating to separate carbonate from cyanides containing electrolytes [146]. Some of the physical properties of these compounds are listed in Table 5.

**Production.** The alkaline earth metal cyanides can be obtained by reaction of the corresponding metal hydroxides with hydrogen cyanide [5]. However, only liquid calcium cyanide is produced by this method. The resulting product has a brownish color due to polymerization of HCN, liberated by hydrolysis.

The production process of the commercially available solid calcium cyanide is different. Black cyanide is produced by treating calcium carbide with nitrogen gas to give calcium cyanamide. The crude cyanamide is then mixed with sodium chloride and heated in electric furnaces above 1000 °C [149]. The cyanamide is converted into calcium cyanide, which is quenched to produce amorphous flakes. The reaction product is gray-black because of the presence of 1 – 2 % carbon. The cyanide content of the amorphous black cyanide is ca. 45 – 50 % NaCN equivalent. Other constituents are 32 % NaCN, 12 % CaO, 2 – 3 % CaCl<sub>2</sub>, and 2 – 3 % CaNCN.

### 2.3. Heavy-Metal Cyanides

Heavy metals usually form stable, insoluble or sparingly soluble simple cyanides M(CN)<sub>x</sub>, which dissolve in the presence of excess alkali metal cyanide to form stable complex salts [111]:



where  $x = 1 - 3$ ;  $y = 1 - 4$

When dissolved in water, the complex cyanide anions tend to dissociate, and various dissociation equilibria are established. The dissociation properties of the most important heavy-metal cyanides are shown in Table 6.

#### 2.3.1. Iron Cyanides

##### 2.3.1.1. Properties

The most important iron cyanides are the hexacyanoferrate(II), ferrocyanide, [Fe(CN)<sub>6</sub>]<sup>4-</sup>, and the hexacyanoferrate(III), ferricyanide, [Fe(CN)<sub>6</sub>]<sup>3-</sup>, complexes, which have an octahedral configuration. They are among the most stable

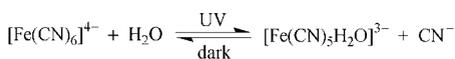
**Table 5.** Physical properties of the alkaline-earth-metal cyanides

Property	Mg(CN) <sub>2</sub> [4100-56-5]	Ca(CN) <sub>2</sub> [592-01-8]	Sr(CN) <sub>2</sub> [52870-08-3]	Ba(CN) <sub>2</sub> [542-62-1]
<i>M<sub>r</sub></i>	76.37	92.12	139.67	189.40
<i>mp</i> , °C		> 350		≈ 600
Decomp., °C	> 300	≈ 640	> 500	> 600
Other crystal forms	Mg(CN) <sub>2</sub> · 2 NH <sub>3</sub>	Ca(CN) <sub>2</sub> · 2 NH <sub>3</sub>	Sr(CN) <sub>2</sub> · 4 H <sub>2</sub> O	Ba(CN) <sub>2</sub> · 2 H <sub>2</sub> O

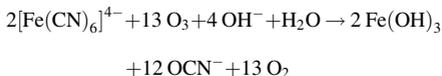
**Table 6.** Stability of heavy-metal cyanide complexes [4, 111]

Dissociation equilibria	$pK_{\text{dissociation}}$
$[\text{Pb}(\text{CN})_4]^{2-} \rightleftharpoons \text{Pb}^{2+} + 4 \text{CN}^-$	10.3
$[\text{Cd}(\text{CN})_4]^{2-} \rightleftharpoons [\text{Cd}(\text{CN})_3]^- + \text{CN}^-$	2.5
$[\text{Cd}(\text{CN})_3]^- \rightleftharpoons \text{Cd}^{2+} + 3 \text{CN}^-$	14.7
$\Sigma$	17.2
$[\text{Zn}(\text{CN})_4]^{2-} \rightleftharpoons [\text{Zn}(\text{CN})_3]^- + \text{CN}^-$	1
$[\text{Zn}(\text{CN})_3]^- \rightleftharpoons \text{Zn}^{2+} + 3 \text{CN}^-$	17.9
$\Sigma$	18.9
$[\text{Ag}(\text{CN})_2]^- \rightleftharpoons \text{Ag}^+ + 2 \text{CN}^-$	20.9
$[\text{Ni}(\text{CN})_4]^{2-} \rightleftharpoons \text{Ni}^{2+} + 4 \text{CN}^-$	$\approx$ 22
$[\text{Cu}(\text{CN})_4]^{3-} \rightleftharpoons [\text{Cu}(\text{CN})_3]^{2-} + \text{CN}^-$	1.5
$[\text{Cu}(\text{CN})_3]^{2-} \rightleftharpoons [\text{Cu}(\text{CN})_2]^- + \text{CN}^-$	5.3
$[\text{Cu}(\text{CN})_2]^- \rightleftharpoons \text{Cu}^+ + 2 \text{CN}^-$	23.9
$\Sigma$	30.7
$[\text{Fe}(\text{CN})_6]^{3-} \rightleftharpoons \text{Fe}^{3+} + 6 \text{CN}^-$	$\approx$ 36
$[\text{Au}(\text{CN})_2]^- \rightleftharpoons \text{Au}^+ + 2 \text{CN}^-$	$\approx$ 37
$[\text{Hg}(\text{CN})_4]^{2-} \rightleftharpoons \text{Hg}^{2+} + 4 \text{CN}^-$	40.5
$[\text{Fe}(\text{CN})_6]^{4-} \rightleftharpoons \text{Fe}^{2+} + 6 \text{CN}^-$	$\approx$ 42
$[\text{Co}(\text{CN})_6]^{4-} \rightleftharpoons \text{Co}^{2+} + 6 \text{CN}^-$	$\approx$ 64
$[\text{Pt}(\text{CN})_4]^{2-} \rightleftharpoons \text{Pt}^{2+} + 4 \text{CN}^-$	$\approx$ 40
$[\text{Pd}(\text{CN})_4]^{2-} \rightleftharpoons \text{Pd}^{2+} + 4 \text{CN}^-$	$\approx$ 42

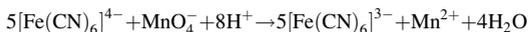
inorganic complexes and are practically nontoxic because of the strong bonding between iron and cyanide (for  $\text{LD}_{50}$  values, see 6). Practically none of the known cyanide reactions can be observed when these compounds are dissolved in water. Only when irradiated with UV light does the hexacyanoferrate(II) ion decompose slowly at normal temperature to form cyanide ions [151]:



In the absence of UV light, only very strong oxidants like ozone are able to oxidize the cyanide and destroy the hexacyanoferrate(II) complex slowly at elevated temperature [152]:

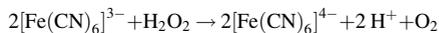
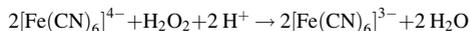


Permanganate, peroxodisulfate, hypochlorite, chlorine, iodine, cesium(IV), and other oxidants oxidize hexacyanoferrate(II) to hexacyanoferrate(III) at moderate temperatures [153], e.g.,

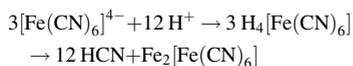


This reaction is used for the determination of hexacyanoferrate (II) in water. Hydrogen peroxide oxidizes hexacyanoferrate(II) to hexacya-

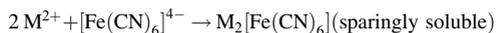
noferrate(III) below pH 3 and reduces hexacyanoferrate(III) to hexacyanoferrate(II) above pH 7:



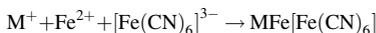
When acidified with mineral acids, solutions of hexacyanoferrates decompose slowly at room temperature and more rapidly when heated, releasing HCN and forming precipitates of iron(II) hexacyanoferrate(II) [14460-02-7] [153]:



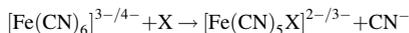
Insoluble or sparingly soluble metal hexacyanoferrates(II) are formed by the addition of aqueous solutions to neutral or weakly acidic solutions of metal salts, particularly heavy metal salts [153]:



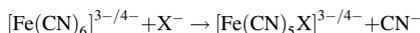
These reactions are used to separate heavy metals from solutions for the purpose of refining and for the production of colored pigments, e.g., Prussian blue pigments, which contain the hexacyanoferrate(III) anion:



Multinuclear complexes are formed by the thermolysis of hexacyanoferrate(II) complexes with complex cations [5]. Many anionic and neutral ligands can be introduced into the hexacyanoferrate anion by substitution of one CN group, to form pentacyano complexes [4, 5].



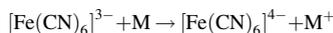
where X = H<sub>2</sub>O, NH<sub>3</sub>, NO, NO<sub>2</sub>, NO<sub>5</sub>, CO



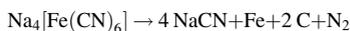
where X = SCN, NCS.

Some of these compounds are used in analytical chemistry. Hexacyanoferrate(II) reacts with a variety of organic amino compounds to form insoluble or slightly soluble salts of general

composition BA, B<sub>3</sub>A<sub>2</sub>, B<sub>2</sub>A, B<sub>3</sub>A, and B<sub>4</sub>A, where B is the cationic nitrogen compound and A the anionic hexacyanoferrate(II) [4]. These reactions are used in analytical and pharmaceutical chemistry. Hexacyanoferrate(III) is a strong oxidant which can dissolve metals; it is used in photographic processes [154] and etching techniques [155]:



The hexacyanoferrates(II) of sodium, potassium, and calcium crystallize with different amounts of water of crystallization, whereas potassium hexacyanoferrate(III) is obtained in anhydrous form. The hexacyanoferrates(II) start to lose water of crystallization above 30 °C and become anhydrous white powders above 80 °C. All hexacyanoferrates decompose above 400 °C to form alkali metal or calcium cyanide, elemental iron, carbon, and nitrogen, e.g.,



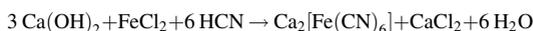
The alkali metal hexacyanoferrates are readily soluble in water; the solubility of the calcium salt is more than twice that of the sodium salt (Table 7). Double salts of low solubility may be formed in the presence of Ca<sup>2+</sup> and K<sup>+</sup> or NH<sub>4</sub><sup>+</sup> ions.

### 2.3.1.2. Production

Historically, the preparation of hexacyanoferrates (II) was based on the fusion of potash with iron compounds and animal residues such as hide, horns, or dried blood, which led to the German name *gelbes Blutlaugensalz* (yellow salt of blood lye). Later, the absorption of hydrogen cyanide from coal gas on iron hydroxide was used to produce hexacyanoferrates. Today, synthetic hydrogen cyanide, iron(II) chloride, and alkali metal

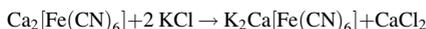
or calcium hydroxide are the raw materials for the large-scale production of hexacyanoferrates(II) on a large scale.

Calcium hexacyanoferrate(II) is usually the primary product, which is subsequently converted to the potassium and sodium salts. Liquid hydrogen cyanide and an aqueous solution of iron (II) chloride are mixed with calcium hydroxide solution in stoichiometric amounts in a stirred reactor:

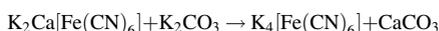


After filtration, the solution is concentrated by evaporation of water under reduced pressure, and the calcium hexacyanoferrate(II) crystallizes with eleven molecules of water of crystallization. The relatively coarse-grained salt is then separated by filtration and generally used without drying. For the conversion of calcium hexacyanoferrate(II) to the potassium or sodium salt, two methods are used.

In the first, a stoichiometric amount of potassium chloride is added to the filtered calcium hexacyanoferrate(II) solution and the hexacyanoferrate(II) precipitates as a sparingly soluble potassium calcium double salt [156]

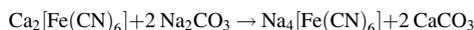


The double salt is separated by filtration, redispersed in water, and then converted to the soluble potassium hexacyanoferrate(II) by the addition of potassium carbonate:



After separation of the insoluble calcium carbonate, the potassium hexacyanoferrate (II) solution is concentrated by evaporation, and the potassium salt crystallizes with three molecules of water of crystallization. After filtration, the salt is carefully dried and packaged.

A similar method can be used for the production of sodium hexacyanoferrate(II): sodium carbonate is added to the calcium hexacyanoferrate(II) solution and the precipitated calcium carbonate is separated:



Usually, the sodium hexacyanoferrate(II) is synthesized directly from solutions of sodium cyanide and iron(II) chloride [157]:



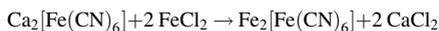
**Table 7.** Solubilities of hexacyanoferrates in water (wt % of anhydrous salt)

Compound	Temperature, °C		
	20	50	80
Na <sub>4</sub> [Fe(CN) <sub>6</sub> ]	16	26	38
K <sub>4</sub> [Fe(CN) <sub>6</sub> ]	22	32	40
Ca <sub>2</sub> [Fe(CN) <sub>6</sub> ]	36	42	44
K <sub>3</sub> [Fe(CN) <sub>6</sub> ]	31	39	45

The crystalline  $\text{Na}_4[\text{Fe}(\text{CN})_6] \cdot 10 \text{H}_2\text{O}$  can be obtained when the solution is concentrated; it must be dried very carefully to avoid loss of water of crystallization, which would influence its solubility properties.

The disadvantages of the double-salt process are the necessity of recycling the various mother liquors and the formation of large quantities of solid waste products.

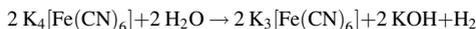
In the second conversion method, the hexacyanoferrate(II) is precipitated from a solution of the calcium salt as Berlin white by the addition of iron(II) chloride solution:



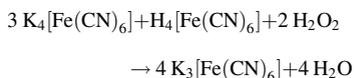
This iron(II) hexacyanoferrate(II) is separated by filtration, redispersed in water, and converted to sodium or potassium hexacyanoferrate(II) by the addition of stoichiometric amounts of sodium or potassium cyanide:



Potassium hexacyanoferrate(III) can be obtained by the oxidation of potassium hexacyanoferrate(II). Usually, anodic oxidation is applied by means of nickel electrodes [158]:



Alternatively, hydrogen peroxide can be used for the oxidation of hexacyanoferrate(II) when the reaction is carried out below pH 3 [159]:



The dry, ruby-red potassium hexacyanoferrate(III) is obtained by concentration of the solution at reduced pressure and crystallization at ca. pH 7. The fact that  $\text{H}_2\text{O}_2$  reduces hexacyanoferrate(III) to hexacyanoferrate(II) at higher pH must also be considered.

### 2.3.1.3. Commercial Forms, Specifications, and Packaging

The following commercial products are most frequently used:

**Sodium hexacyanoferrate(II)** [69043-75-0], sodium ferrocyanide, yellow prussiate of soda (YPS),  $\text{Na}_4[\text{Fe}(\text{CN})_6] \cdot 10 \text{H}_2\text{O}$ ,  $M_r$  484.108,  $\rho$  1.46 g/cm<sup>3</sup>, light yellow, monoclinic crystals,

readily soluble in water (33.7 g in 100 g  $\text{H}_2\text{O}$  at 20 °C).

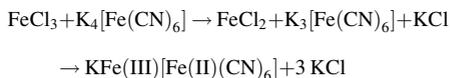
**Potassium Hexacyanoferrate(II)** [14459-95-1], potassium ferrocyanide, yellow prussiate of potash (YPP),  $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3 \text{H}_2\text{O}$ ,  $M_r$  422.39,  $\rho$  1.85 g/cm<sup>3</sup>, lemon yellow, monoclinic crystals, readily soluble in water (33.7 g in 100 g  $\text{H}_2\text{O}$  at 20 °C).

**Calcium Hexacyanoferrate(II)** [13821-08-4], calcium ferrocyanide, yellow prussiate of calcium (YPC),  $\text{Ca}_2[\text{Fe}(\text{CN})_6] \cdot 11 \text{H}_2\text{O}$ ,  $M_r$  490.296,  $\rho$  1.68 g/cm<sup>3</sup>, yellow monoclinic crystals, highly soluble in water (148.4 g in 100 g  $\text{H}_2\text{O}$  at 20 °C).

**Potassium Hexacyanoferrate(III)** [13746-66-2], potassium ferricyanide,  $\text{K}_3[\text{Fe}(\text{CN})_6]$ ,  $M_r$  329.25,  $\rho$  1.858 g/cm<sup>3</sup>, orange to ruby red, monoclinic crystals, readily soluble in water (46.4 g in 100 g  $\text{H}_2\text{O}$  at 20 °C).

The commercial products are fine, crystalline, free-flowing powders. Normally, they are packaged in polyethylene bags of 25-kg net weight, and must be stored under cool, dry conditions and kept away from acids. Hexacyanoferrates are not dangerous goods according to appendix C of the EVO, GGVS, RID, ADR, and IMCO Code. The specifications and average analyses for the commercially used hexacyanoferrates are listed in Table 8.

**Uses and Economic Aspects.** Sodium, potassium, and calcium hexacyanoferrates(II) are equally suitable for use in most applications, but sometimes one product may be preferred. For the production of blue pigments, the most important application of hexacyanoferrates, the potassium salt is used in Europe, whereas the sodium salt is preferred in the United States. Generally, blue hexacyanoferrate(II) compounds are formed by the reaction of iron(III) salts with hexacyanoferrates(II):



The production of blue pigments is more complicated, however, and is based primarily on the oxidation of iron(II) hexacyanoferrate(II) precipitates in the presence of alkali metal or

**Table 8.** Specifications of hexacyanoferrates

	Na <sub>4</sub> [Fe (CN) <sub>6</sub> ] · 10 H <sub>2</sub> O (anticaking of NaCl)	K <sub>4</sub> [Fe (CN) <sub>6</sub> ] · 3 H <sub>2</sub> O (refining of wine)	Ca <sub>2</sub> [Fe (CN) <sub>6</sub> ] · 11 H <sub>2</sub> O (anticaking of NaCl)	K <sub>3</sub> [Fe (CN) <sub>6</sub> ] (photographic industry*)
Assay, %	> 99.0	> 99.0	> 99.5	> 98.5
[Fe (CN) <sub>6</sub> ] <sup>4-</sup> , %	> 43.3	> 49.7	> 43.0	< 0.5
H <sub>2</sub> O, %	< 37.5*	< 12.0	< 41*	< 0.1
Ca + Mg, mval		< 60		
Cl <sup>-</sup> , %	< 0.2	< 0.02	< 0.6*	< 0.25
SO <sub>4</sub> <sup>2-</sup> , %	< 0.07	< 0.005	< 0.01*	< 0.1
CO <sub>3</sub> <sup>2-</sup> , %	< 0.15*	< 0.1*	< 0.05*	
S <sup>2-</sup> , ppm		< 100		
NH <sub>3</sub> , ppm		< 100		
Heavy metals, as				
Pb, ppm	< 10	< 10	< 10	
Zn, ppm	< 25	< 10	< 25	
As, ppm	< 3	< 1	< 3	
HCN, ppm		< 100		
Insolubles, %	< 0.03	< 0.01	< 0.1*	< 0.05
pH (10 % solution)	10 – 11*	10 – 11*	10 – 11*	6 – 8

\* Average analysis.

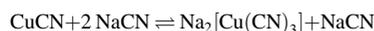
ammonium salts [2]. The properties of blue pigments are not dependent only on the composition; the precipitation method and the finishing of the product are also very important. The use of hexacyanoferrates(II) for the production of classified documents is also based on this reaction. Large amounts of all three types of hexacyanoferrates (II) are used as additives for rock salt to prevent caking [160]; hexacyanoferrates(II) act as crystal growth inhibitors in this application. The ability of hexacyanoferrates(II) to form insoluble or almost insoluble heavy metal compounds is used, e.g., in the production of citric acid by fermentation [161], in the refining of wine [162], in the electroplating of tin [163], and in analytical chemistry. Potassium hexacyanoferrate(III) and alkali hexacyanoferrate(II) combined with peroxodisulfates play an important role as bleaching agents in color photography [154]. Both hexacyanoferrates are also important depressants for the separation of molybdenum from copper by flotation [164].

### 2.3.2. Cyanides of Copper, Zinc, and Cadmium

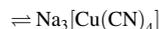
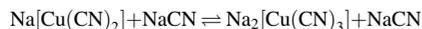
#### Properties.

*Copper(I) Cyanide* [544-92-3], CuCN,  $M_r$  89.56,  $mp$  473 °C, forms white monoclinic prismatic crystals,  $\rho$  2.92 g/cm<sup>3</sup>, which are insoluble

in water, dilute mineral acids, and organic solvents; CuCN is soluble in ammonia and in alkali metal cyanide solution because equilibria are established with highly soluble cyano complexes:



(slightly soluble) (slightly soluble)



(slightly soluble)

These complexes can also be obtained as solids. In the absence of air and moisture, pure CuCN can be stored indefinitely without deterioration.

*Zinc Cyanide* [557-21-1], Zn (CN)<sub>2</sub>,  $M_r$  117.42,  $mp$  800 °C (decomp.), forms a white crystalline powder with a slight HCN odor,  $\rho$  1.852 g/cm<sup>3</sup> (25 °C), which is insoluble in water but soluble in aqueous solutions of alkali metal hydroxides or cyanides by formation of hydroxy ([Zn (OH)<sub>4</sub>]<sup>2-</sup>) or cyano complexes ([Zn (CN)<sub>4</sub>]<sup>2-</sup>). In the absence of air, carbon dioxide, and moisture, zinc cyanide can be stored indefinitely without deterioration.

*Cadmium Cyanide* [542-83-6], Cd (CN)<sub>2</sub>,  $M_r$  164.45,  $mp$  200 °C (decomp.), forms white

**Table 9.** Specifications (DIN 50971) and average analysis of the cyanides of copper, zinc, and cadmium

	CuCN		Zn (CN) <sub>2</sub>		Cd (CN) <sub>2</sub>	
	DIN 50 971	Average analysis	DIN 50 971	Average analysis	DIN 50 971	Average analysis
Cu <sup>+</sup> , %	> 70.0	> 70.0	< 0.001	< 0.001	< 0.001	< 0.001
Zn <sup>2+</sup> , %	< 0.002	< 0.002	> 55.0	> 55	< 0.005	< 0.005
Cd <sup>2+</sup> , %	< 0.001	< 0.001	< 0.005	< 0.005	> 67.0	> 67.0
CN <sup>-</sup> , %	> 28.8	> 28.8	> 42.0	> 43	> 30.0	> 30.0
OH <sup>-</sup> , %		< 0.05	< 0.05		< 0.05	
CO <sub>3</sub> <sup>2-</sup> , %		< 0.1	< 0.5			
Cl <sup>-</sup> , %		< 0.1	< 0.1		< 0.1	
SO <sub>4</sub> <sup>2-</sup> , %		< 0.1	< 0.3		< 0.5	
H <sub>2</sub> O, %		< 0.1	< 0.5		< 0.5	
Sb, ppm	< 10	< 10	< 10	< 10	< 100	< 100
As, ppm	< 10	< 10	< 10	< 10	< 100	< 100
Pb, ppm	< 20	< 20	< 50	< 50	< 50	< 50
Fe, ppm	< 100	< 100	< 100	< 100	< 500	< 500
Ni, ppm	< 20	< 20	< 50	< 50	< 50	< 50
Sn, ppm	< 10	< 10	< 10	< 10	< 100	< 100
Insoluble in NaCN solution, %	< 0.02	< 0.02	< 0.1	< 0.1	< 0.1	< 0.1

irregular octahedral crystals,  $\rho$  2.23 g/cm<sup>3</sup> (25 °C), which are soluble in water (1.7 g in 100 g H<sub>2</sub>O at 15 °C). Cyano complexes are formed when cadmium cyanide is dissolved in aqueous solutions of alkali metal cyanides: [Cd (CN)<sub>3</sub>]<sup>-</sup>, [Cd (CN)<sub>4</sub>]<sup>2-</sup>. In the absence of air and moisture, pure Cd (CN)<sub>2</sub> is stable and can be stored indefinitely; in moist air, it decomposes slowly.

**Production.** The preferred method for the production of copper cyanide is based on the reaction of copper(II) salts, metallic copper, and hydrogen cyanide in hydrochloric acid solution [165, 166]. The reaction solution can be recycled, which avoids environmental problems. The Cu (CN)<sub>2</sub> formed when copper(II) salts react directly with alkali cyanide or HCN is unstable and decomposes to CuCN and cyanogen, (CN)<sub>2</sub> (see Section 5.2).

Zinc cyanide can be obtained from the reaction of zinc salts with alkali cyanide in aqueous solution. However, the reaction of zinc oxide with hydrogen cyanide in acetic acid has the advantage that no additional salt is produced [167].

Cadmium cyanide can be produced by evaporation of a solution of cadmium hydroxide in aqueous hydrogen cyanide [168] or by precipitation from a cadmium salt solution with alkali cyanide [169].

**Commercial Forms, Specifications, and Packaging.** Commercially, CuCN and Zn

(CN)<sub>2</sub> are supplied as white, fine crystalline powders, packaged in steel drums of 10 kg, 25 kg, and 50 kg net weight. Also 1 t packages, as described for the alkali metal cyanides are available. The specifications and the average analyses are shown in Table 9.

Water-soluble, complex copper and zinc cyanides, as well as mixtures of CuCN and Zn (CN)<sub>2</sub> with alkali metal cyanides (containing ca. 23 or 29 % Cu or 23 % Zn), are available for use in electroplating processes.

For transportation, storage, and handling, the same precautions must be observed as for alkali metal cyanides.

**Uses and Economic Aspects.** The simple cyanides of copper and zinc are used primarily in combination with alkali metal cyanides in bath formulations for the electroplating industry. The main applications are copper, zinc, and brass plating.

Copper(I) cyanide is an important reagent for the introduction of cyano groups into aromatic rings to produce benzonitrile derivatives (Sandmeyer reaction). Furthermore, it is used in the synthesis of insecticides and fungicides [170], in the preparation of special paints for ships, as a catalyst for the polymerization of organic compounds, and for the synthesis of anticancer drugs. Copper and zinc cyanide are used in the production of phthalocyanine dyes.

### 2.3.3. Cyanides of Mercury, Lead, Cobalt, and Nickel

The cyanides of mercury, lead, cobalt, and nickel do not have any major industrial importance. Water-soluble complex cyanides can be obtained by the reaction of the simple cyanides with alkali metal cyanides.

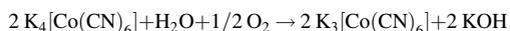
#### Properties, Preparation, and Uses.

**Mercury(II) Cyanide** [3021-39-4],  $\text{Hg}(\text{CN})_2$ ,  $M_r$  252.65,  $\rho$  4.0 g/cm<sup>3</sup>, forms white crystals, which are very soluble in water; it is highly toxic. The substance can be prepared by the reaction of  $\text{HgO}$  with aqueous  $\text{HCN}$ . When heated, it decomposes to  $\text{Hg}$  and  $(\text{CN})_2$ , and may explode if detonated [168, 171]. The complex salts  $\text{Na}[\text{Hg}(\text{CN})_3]$ ,  $M_r$  301.66, and  $\text{K}_2[\text{Hg}(\text{CN})_4]$  [591-89-9],  $M_r$  382.87, are white crystalline powders which are very soluble in water. Mercury (II) oxide cyanide [2040-54-2],  $\text{Hg}(\text{CN})_2 \cdot \text{HgO}$ ,  $M_r$  469.26, is less stable and more sensitive to shock than picric acid [172].

**Lead Cyanide** [13453-58-2],  $\text{Pb}(\text{CN})_2$ ,  $M_r$  259.25, can be obtained by the reaction of aqueous solutions of lead salts and alkali metal cyanides in the presence of  $\text{HCN}$  [2]. In the absence of  $\text{HCN}$ , oxide cyanides are formed, e.g.,  $\text{Pb}(\text{CN})_2 \cdot 2 \text{PbO}$ .

**Cobalt(II) Cyanide** [542-84-7],  $\text{Co}(\text{CN})_2 \cdot 2 \text{H}_2\text{O}$ ,  $M_r$  110.95,  $mp$  280 °C (decomp.),  $\rho$  1.872 g/cm<sup>3</sup>, forms red-brown needles which are insoluble in water. It can be obtained by the reaction of aqueous solutions of cobalt salts and alkali metal cyanides, and can be converted to soluble complex compounds with ammonia or excess alkali metal cyanide.

Complex cobalt(III) cyanides are formed when solutions of complex cobalt(II) cyanides are heated in the presence of oxygen:



Cobalt cyanides are among the most stable complexes; therefore, cobalt compounds have been used as antidotes for cyanide poisoning [173].

**Nickel Cyanide** [557-19-7],  $\text{Ni}(\text{CN})_2$ ,  $M_r$  110.74,  $mp > 200$  °C (decomp.),  $\rho$  2.393 g/cm<sup>3</sup>,

forms brownish-yellow crystals which are insoluble in water. It can be obtained by the dehydration of  $\text{Ni}(\text{CN})_2 \cdot 4 \text{H}_2\text{O}$ , which is precipitated when alkali metal cyanide is added to a solution of a nickel salt.

Potassium tetracyanonickelate(II) monohydrate [14323-41-2],  $\text{K}_2[\text{Ni}(\text{CN})_4] \cdot \text{H}_2\text{O}$ ,  $M_r$  258.97, forms orange-red crystals which are very soluble in water. The complex salt is formed when excess  $\text{KCN}$  is employed in the preparation;  $\text{K}_2[\text{Ni}(\text{CN})_4]$  is used as an additive to electrolytes in the plating of gold, silver, and zinc, to improve the quality of the deposits.

### 2.3.4. Cyanides of Precious Metals

The precious metal cyanides can be regarded as the historical starting point of inorganic cyanide chemistry. Their importance for the recovery, refining, and electroplating of precious metals is as great today as it was 100 years ago.

**Gold(I) Cyanide** [506-65-0],  $\text{AuCN}$ ,  $M_r$  222.98,  $\rho$  7.12 g/cm<sup>3</sup>, forms yellow crystals which are insoluble in water and hot dilute acids, but soluble in ether, alkali metal hydroxide, and thiosulfate solutions. Water-soluble  $[\text{Au}(\text{CN})_2]^-$  complexes are formed when  $\text{AuCN}$  is dissolved in alkali metal cyanide solution or when gold metal is attacked by alkali metal cyanide in the presence of oxygen or oxidizing agents.

**Silver(I) Cyanide** [506-64-9],  $\text{AgCN}$ ,  $M_r$  133.89,  $mp$  320 °C (decomp.),  $\rho$  3.95 g/cm<sup>3</sup>, forms white hexagonal crystals which are insoluble in water but soluble in aqueous alkali metal cyanide solution, forming complex  $[\text{Ag}(\text{CN})_2]^-$  compounds. Like  $\text{AgCl}$ ,  $\text{AgCN}$  becomes brown if exposed to light. The production of  $\text{AgCN}$  is based on the reaction of  $\text{AgNO}_3$  with alkali metal cyanide in aqueous solution. Its main application is in electroplating.

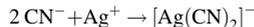
**Palladium(II) Cyanide** [2035-66-7],  $\text{Pd}(\text{CN})_2$ ,  $M_r$  158.7,  $mp$  210 °C (decomp.), is soluble in water.

**Platinum(II) Cyanide** [592-06-3],  $\text{Pt}(\text{CN})_2$ ,  $M_r$  247.27, is insoluble in water and

dilute acids. Both palladium(II) cyanide and platinum(II) cyanide can be prepared from the corresponding chlorides by precipitation with  $\text{Hg}(\text{CN})_2$ . Tetracyano complexes are formed with excess alkali metal cyanide:  $\text{K}_2[\text{Pd}(\text{CN})_4] \cdot 3 \text{H}_2\text{O}$  forms white rhombohedral fluorescent crystals, and  $\text{K}_2[\text{Pt}(\text{CN})_4] \cdot 3 \text{H}_2\text{O}$  forms rhombic yellow prisms with blue fluorescence. The barium salt  $\text{Ba}[\text{Pt}(\text{CN})_4] \cdot 4 \text{H}_2\text{O}$  is used to prepare the fluorescent coating of X-ray screens; the alkali metal tetracyanoplatinates are used in electroplating. The unstable  $\text{Pd}(\text{CN})_4$  is also known.

## 2.4. Cyanide Analysis

The cyanide content of solid alkali metal cyanides, alkaline earth metal cyanides, and dissociating heavy metal cyano complexes such as  $[\text{Zn}(\text{CN})_4]^{2-}$  may be determined by the argentometric titration of a dilute aqueous solution of the cyanide, according to the method of Liebig – Denigés, in which potassium iodide is used as an indicator [174]:



A very accurate indication of the end point of this reaction can be obtained potentiometrically by using a silver – calomel or silver – Thalamide (Schott Glaswerke, Mainz) electrode pair. This method of determination is called the determination of free cyanide and is also an important parameter in the leaching of gold and silver ores.

For more stable cyano complexes or insoluble cyanide compounds [e.g., iron(II) hexacyanoferrate(II)] or in the presence of substances that disturb the argentometric titration, liberation and separation of the cyanide must be carried out before determination. This can be done by acidifying and boiling the cyanide solution or suspension, and absorbing the released hydrogen cyanide in sodium hydroxide solution [175]. Depending on the concentration, the cyanide content of the absorption solution may be analyzed argentometrically or colorimetrically, e.g., by using pyridine-barbituric acid reagents [176]. This method of determination is called the determination of total cyanide, because all except extremely stable cyanide complexes,

such as that of cobalt, liberate cyanide for determination. There is an ISO standard for total cyanide determination (ISO/DIS 6703/1) [177]. The ASTM determination method for total cyanide is also used internationally [178].

To evaluate the toxicity of wastewaters and effluents that contain cyanide, readily liberable cyanide (ISO/DIS 6703/1) is a reliable method for determining less stable complexes of cyanide. Hydrogen cyanide, alkali and alkaline earth metal cyanides, and the cyanides of zinc, cadmium, silver, mercury, copper, and nickel are determined by this method. The complex cyanides of iron, cobalt, gold, and nitriles [177] are not amenable to this method. In this method, hydrogen cyanide is liberated at pH 4 in the presence of zinc metal and ethylenediaminetetraacetic acid. The HCN is transferred to an absorption vessel and analyzed argentometrically or colorimetrically. The ASTM method for the determination of less stable complexes of cyanide is called the weak acid-dissociable cyanide method [178]. Another fast determination method of cyanide analysis, similar to the above two distillation methods, is the colorimetric picric acid method [179]. This method has gained in popularity since the 1970s, it yields very similar results to the above two standard methods but is much quicker. This is important, where effluents are discharged continuously (e.g., gold mine effluent).

Other cyanide determination methods such as the colorimetric method with pyridine – barbituric acid reagents [176] and ion-selective electrode [180] methods for free cyanide are prone to interference by various substances. The ion-chromatographic method has been a subject of research since the 1980s, and techniques have been developed to determine several cyanide species selectively, especially at low concentrations. However, these techniques and instrumentation have not yet achieved widespread application [180].

Quick tests to check the concentration of cyanides in wastewater are based on various colorimetric methods [176, 179]. Generally, the reactions permit detection of very small amounts of free cyanide, but they can be disturbed by various substances, e.g., reducing agents or thiocyanate, sulfide, and nitrite, which all produce similar colors.

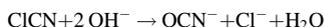
### 3. Detoxification of Cyanide-Containing Wastes

Whenever cyanides are manufactured or used, effluents and wastes containing various amounts of cyanide are produced. Because of the high toxicity of cyanide to all forms of life (see Chap. 6), the effluents and wastes must be treated to reduce the cyanide content to concentrations that are acceptable with the regard to the particular environmental conditions [181–185]. Depending on the quantity and type of cyanidic waste, various detoxification methods are used [186–190]. In addition to effectiveness and cost of treatment, the formation of undesirable byproducts and additional salting of the wastewater are factors of growing importance in choosing an effluent-treatment method.

Heavy metals may be precipitated and separated as hydroxides, carbonates, or sulfides, when complex heavy metal cyanides are oxidized. Wastewater treatment can be carried out batchwise or continuously, and the process may be monitored and controlled automatically.

#### 3.1. Wastewater Treatment

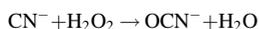
**Chlorination.** Alkaline chlorination is the most frequently used process for the treatment of effluents containing  $< 1 \text{ g CN}^-$  per liter [191]. In principle, this method allows the destruction of all commercially used simple and complex cyanides, with the exception of complex iron cyanides, which are only attacked above  $80^\circ\text{C}$ . The treatment can be carried out with chlorine and alkali [ $\text{NaOH}$ ,  $\text{Ca}(\text{OH})_2$ ] or with readymade hypochlorite solutions that contain about 12%  $\text{NaOCl}$ . At first, toxic cyanogen chloride is formed, which is hydrolyzed quickly to cyanate and chloride at  $\text{pH} > 11$  [192]:



Additional salting of the water is the main disadvantage of alkaline chlorination: at least 5 kg of  $\text{NaCl}$  is produced per kilogram of cyanide for the oxidation of cyanate, and an additional 6.5 kg of  $\text{NaCl}$  per kilogram of cyanide results from total oxidation [193]. Alkaline chlorination

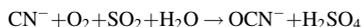
is frequently used for the treatment of smaller quantities of effluent and less for large continuous operations. It is frequently used, for example, in the detoxification of electroplating effluents, when permissible. Lower chloride limits in the treated effluent make an alternative process necessary. Hypochlorite solutions tend to lose their active oxygen content relatively fast.

**Hydrogen Peroxide Oxidation.** The use of hydrogen peroxide for cyanide detoxification has increased because, in this case, the oxidation of cyanide leads directly to cyanate without the formation of toxic intermediates and byproducts, and the oxidant does not cause additional salting [193, 194]:

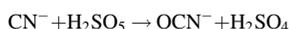


The  $\text{H}_2\text{O}_2$  process is used mainly for the batchwise treatment of effluents from organic nitrile synthesis and metal hardening plants, and can be monitored and controlled automatically [195, 196]. One process allows delivery of accurate amounts of  $\text{H}_2\text{O}_2$  to continuous effluent streams, which is controlled by on-line measurement of the total oxygen demand [197]; this process is used, for example, in the treatment of tailings from gold mines [180, 198]. More recently, the  $\text{H}_2\text{O}_2$  process has increasingly found applications in the seasonal detoxification of effluents from gold mines, because of the ease of operation and relatively low investment costs. The  $\text{H}_2\text{O}_2$  process has been optimized by the addition of compounds that reduce the quantity of  $\text{H}_2\text{O}_2$  required [199].

**Other Methods of Treatment.** A method from 1982 is based on the treatment of effluents with a mixture of sulfur dioxide (2.5%) and air in the presence of small amounts of copper salts ( $> 50 \text{ mg Cu}$  per liter) as catalyst [205]:



This is called the Inco process. The detoxification of cyanide-containing pulps is becoming more and more important. In addition to the Inco process method above, the Caro's acid process is also used to treat cyanide-containing pulps according to the reaction:



A further development uses the synergies between the Inco process and the Caro's acid or hydrogen peroxide process to detoxify cyanide-containing slurries more efficiently. This process is called the CombiOx process [206].

In the case of highly concentrated cyanide solutions, the volatilization and catalytic oxidation of HCN after acidification of the solutions can be used [189]. Sometimes, the hydrogen cyanide can be reused by absorption in alkali metal hydroxide solution and conversion to alkali metal cyanide. Atmospheric oxygen is occasionally used for the destruction of cyanide in weak solutions, in combination with activated carbon [101, 201] or microorganisms [202]. Removal of cyanides by ion exchange and reverse osmosis does not solve the problem entirely because the concentrates require further treatment [203, 204].

The hydrolysis of cyanide at 180 – 230 °C under pressure can be used for the destruction of simple and complex cyanides, even in high concentrations [98]. The process does not require chemicals, but the investment for the plant is high.

The conversion of cyanide to thiocyanate by the addition of sulfur is a process that used to be employed but is now regarded more critically [186]. This process has the advantage of low reagent costs, but the investment for plant can be high. It is less suitable for seasonal detoxification, since start up and decommissioning can take time.

Very effective oxidation of cyanide to cyanate, carbonate, and nitrogen takes place with ozone [98, 200]; however, this requires high capital investment and causes problems with the adaptation to varying oxygen demand.

The conversion of cyanide to hexacyanoferrate(II) by reaction with iron(II) salts in alkaline solution followed by precipitation of hexacyanoferrate(II) as iron(II) hexacyanoferrate(II) at pH 3 – 4 is one of the oldest methods for cyanide removal [207]. However, this should be used only for the removal of complex iron cyanides, if at all, because the sludge must be disposed of in such a manner that water resources are protected. Furthermore, the filtrates must be treated again to destroy the remaining traces of cyanide.

In many cases, low concentrations of complex iron cyanides (e.g., < 20 mg of cyanide

per liter) in effluents discharged to sewage systems are tolerated because they are precipitated in contact with metal salts (e.g., the iron salts present in domestic wastewater) and are separated with the sludge of municipal sewage treatment plants.

### 3.2. Solid Wastes

For a long time, disposal of the solid wastes from metal hardening plants, which contain alkali metal cyanides, cyanates, nitrites, and nitrates in addition to other inorganic salts, was a special problem [88, 89]. New processes have been developed that, in many cases, allow regeneration of waste salts. In any case, solid wastes should not be treated or destroyed by a wet chemical process. The safest and most practical solution to the disposal problem at the present time is to deposit them in disused salt mines.

## 4. Cyanogen Halides

Halogen cyanides, usually known as cyanogen halides, have been the subject of considerable interest, and some aspects of their chemistry have been reviewed in detail [2, 6–11]. These compounds, except for cyanogen fluoride, have been known for a long time [208, 209]. Cyanogen fluoride was prepared in 1981 [210, 211]. Depending upon the electronegativity of the halogens relative to the cyanide group, the cyanogen halides can act as halogenating or cyanating agents. The cyanogen halides can be regarded as pseudohalogen or interhalogen compounds with a definite nitrile structure ( $X-C\equiv N$ ) [212]. The most important cyanogen halide is cyanogen chloride, which is used for the commercial production of cyanuric chloride, a starting material for pesticides, dyes, and drugs ( $\rightarrow$  Cyanuric Acid and Cyanuric Chloride).

### 4.1. Properties

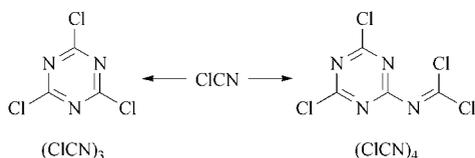
**Physical Properties.** The pure cyanogen halides are colorless, highly volatile, and poisonous compounds. Some physical properties are given in Table 10.

**Table 10.** Physical properties of the cyanogen halides [10, 11, 212]

	FCN [1495-50-7]	CICN [506-77-4]	BrCN [506-68-3]	ICN [506-78-5]
$M_r$	45.02	61.47	105.92	152.92
$mp$ , °C	- 82	- 6.5	52	148*
$bp$ , °C	- 46.2	12.5	61	subl. > 45*
Density $\rho$ , g/cm <sup>3</sup>		1.24 (0 °C) 1.19 (15 °C)	2.01 (18 °C) 1.18 (54 °C)	2.84 (18 °C)
Bond length, pm				
C–Hal	126.0	162.9	179.0	199.5
C–N	116.5	116.3	115.8	115.9
Enthalpy of vaporization $\Delta H_v$ , kJ/mol	22.39	26.75	33.82	40.02
Enthalpy of fusion $\Delta H_f$ , kJ/mol		11.39		19.88
Enthalpy of sublimation $\Delta H_s$ , kJ/mol			45.21	59.90
Dipole moment $\mu$ , D	2.17	2.80	2.94	3.71

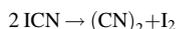
\*Triple point,  $p = 132.1$  kPa; subl. = sublimation.

**Chemical Properties.** Pure cyanogen halides are stable at normal temperature. Impurities catalyze the exothermic trimerization to the corresponding cyanuric halides. Catalysts are proton acids, Lewis acids (e.g., heavy metal salts), and bases. Relatively little is known about the preparative use of FCN [211], which explodes at - 41 °C on ignition. Mixtures of FCN and air are more explosive than mixtures of acetylene and air [213]. In a catalytic reaction, CICN forms not only the trimer (cyanuric chloride [108-77-0]) but also a stable tetramer, 2,4-dichloro-6-isocyanodichloro-*s*-triazine [877-83-8] [214].



Cyanogen bromide polymerizes more readily to cyanuric bromide [14921-00-7] than does CICN to cyanuric chloride [215].

When heated to 130 °C in a sealed tube, cyanogen iodide does not polymerize [216]. Above 150 °C, ICN eliminates iodine:



The reaction is not reversible [217].

Cyanogen chloride is an intermediate in the detoxification of cyanide-containing wastewater with sodium hypochlorite solutions; therefore, the cyanogen halide must be removed immediately by appropriate hydrolysis [218]. Alkaline

hydrolysis of cyanogen halides proceeds in different ways:



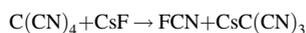
Thus, CICN and BrCN are hydrolyzed to the cyanate and halide salts; ICN, however, forms hypoiodite, which disproportionates to iodide and iodate. This is due to the more electropositive character of iodine relative to chlorine [11]. Therefore, CICN can be used for the electrophilic introduction of a cyano group into a substrate; use of ICN results in electrophilic iodination. The reaction pathway of BrCN often depends on the reaction conditions and on the nature of the substrate [219]. Cyanogen halides add to olefins and acetylenes in the presence of acid catalysts [220, 221]. Aromatic ring systems can be cyanated by CICN or BrCN under Friedel – Crafts conditions [212, 223]. The reactions of cyanogen halides, particularly CICN and BrCN, with nitrogen, oxygen, and sulfur nucleophiles lead to cyanamides [224–226] cyanates [227, 228], and thiocyanates [229].

In some cases, the newly formed compound undergoes further reactions at the  $\text{C}\equiv\text{N}$  triple bond to form guanidines [224, 225], ureas, or heterocyclic ring systems [230]. Cyanogen bromide reacts with tertiary alkylamines to form ammonium bromides, which decompose to give dialkyl cyanamides and alkyl bromides (von Braun reaction) [231, 232]. Reaction of sulfur trioxide with CICN leads to the very reactive

chlorosulfonyl isocyanate [233, 234]. Cyanogen halides undergo radical reactions at elevated temperatures on irradiation with UV light or in the presence of peroxide promoters. Thus, cyanogen chloride and acetonitrile are converted to malonodinitrile [235–238]. In the gas phase, aromatic methyl compounds and cyanogen chloride react to give arylacetonitriles [239].

## 4.2. Production

Cyanogen fluoride is prepared by the reaction of tetracyanomethane with cesium fluoride [240]:



The pyrolysis of cyanuric fluoride at 1300 °C under reduced pressure gives FCN in ca. 50 % yield [210, 211, 213].

The preparation of the industrially important ClCN has been developed extensively; the synthetic pathways are as follows:

1. Electrolysis of an aqueous solution of HCN and  $\text{NH}_4\text{Cl}$  [241]
2. Reaction of complex cyanide salts (e.g.,  $\text{Na}_2[\text{Zn}(\text{CN})_4]$ ) with chlorine below 20 °C [242]
3. Formation of ClCN from cyanide salts (mostly NaCN) and chlorine in an exothermic reaction; in a continuous process, sprayed aqueous NaCN solution is contacted with chlorine, and the reaction heat evaporates the ClCN [243].
4. Processes involving hydrogen cyanide and chlorine as the most convenient starting materials; the reaction is carried out in aqueous solution [244–249] (for a detailed procedure, see also → Cyanuric Acid and Cyanuric Chloride) in organic [250] and inorganic solvents [251], and in the gas phase [252, 253]. To avoid the byproduct HCl, attempts have been made to reoxidize HCl to chlorine with oxygen [248] and hydrogen peroxide [254, 255] in catalyzed reactions.
5. Chlorinolysis of cyanogen in the gas phase at 300 – 600 °C in the presence of a catalyst [256, 257]
6. Pyrolysis of cyanuric chloride at 600 – 900 °C in the presence of a charcoal catalyst [258]
7. High-temperature syntheses based on elemental chlorine, nitrogen, and carbon [259]

Usually, these processes lead to impure ClCN; therefore, in many cases the product must be purified before further use. Water can be removed by treatment with calcium salts or molecular sieves and by fractional distillation [260]. Chlorine is stripped with water (mixed with HCN and HCl) [261] or with solutions containing a soluble iron(II) salt and an insoluble carbonate [262]; chlorine may also be eliminated by treatment with  $\gamma$ -aluminum oxide [263]. Cyanogen chloride, free of HCl, is obtained by treatment with water [261] or with organic solvents [264, 265]. Hydrogen cyanide is removed by distillation with chlorine [266] or by washing with  $\text{FeSO}_4$  solutions [267].

Cyanogen bromide can be prepared from bromine and cyanide salts or hydrogen cyanide [268, 269]. Cyanogen iodide is synthesized analogously [270, 271].

## 4.3. Storage and Transportation

In most cases, ClCN is used in the gas phase immediately after preparation. Relatively small amounts are condensed and stored in gas containers as liquids. Steel cylinders, which must meet specific requirements in each country, can be used for shipment. The condensed and bottled ClCN must be very pure; moreover, it must be mixed with a stabilizing agent (generally sodium pyrophosphate) to inhibit exothermic polymerization caused by impurities [272–274]. Impure BrCN can polymerize during storage [275]; the danger of explosion exists with closed BrCN bottles [276]. Cyanogen halides should be handled carefully because they are very toxic (similar to HCN) and have a strong lacrimatory effect.

## 4.4. Uses

Most of the cyanogen chloride is used for the production of cyanuric chloride. The reaction with amines leads to diphenylguanidines (vulcanization accelerators) [277]. Cyanogen chloride and bisphenols react to give cyanate esters, which can polymerize to polytriazine resins [227, 228].

Halogen cyanides and cyanamide react to form dicyanamide [504-66-5] [278, 279], which is used for the preparation of pharmaceutical

bisbiguanides. The industrial production of malonodinitrile [109-77-3] [235–238], and chlorosulfonyl isocyanate [1189-71-5] [233, 234] based on cyanogen chloride has become increasingly important. Cyanogen chloride is the most economically significant of all cyanogen halides. Its worldwide production capacity is more than 230 000 t/a (mainly in Europe and the United States).

Cyanogen bromide and cyanogen iodide are commonly used in the laboratory, e.g., for the dealkylation of tertiary amines [231, 232], the selective cleavage of peptides [280], and the preparation of heterocyclic compounds.

## 5. Cyanogen

The first synthesis of cyanogen [460-19-5], dicyanogen, oxalonitrile, (CN)<sub>2</sub>, *M<sub>r</sub>* 52.05, was carried out by GAY-LUSSAC in 1815 by pyrolysis of silver cyanide [267]. The chemistry of this reactive compound is discussed in [1, 12–17]. In many respects, cyanogen can be compared to the halogens. In addition, many of its properties are a result of the reactivity of the cyano groups. Although various procedures for the synthesis of cyanogen are known, commercial interest in cyanogen is limited.

### 5.1. Properties [1, 17]

**Physical Properties.** At room temperature, cyanogen is a colorless, flammable, and very poisonous gas with a pungent odor. Some important physical properties are listed below:

Melting point	–27.98 °C
Boiling point	–21.15 °C
Critical pressure, <i>p<sub>crit</sub></i>	60.79 bar
Critical temperature, <i>t<sub>crit</sub></i>	128.3 °C
Density	2.321 g/L at 0 °C 1.25 g/cm <sup>3</sup> at –95 °C 0.954 g/cm <sup>3</sup> at –21.17 °C

Vapor pressure					
<i>t</i> , °C	–21.15	–4.88	20.88	44.43	72.40
<i>p</i> , bar	1	2	5	10	20

Solubility at 20 °C: water dissolves 4.5 times its own volume of cyanogen; diethyl ether, 5.0 times; and ethanol, 23.0 times.

Bond length:	
C–C	138 pm
C–N	113 pm
Bond angle: C–C–N	
	179° 38'
Enthalpy of fusion, $\Delta H_f$	
	8.112 kJ/mol
Enthalpy of vaporization	
	23.341 kJ/mol
MAK	
	10 ppm

The values reported for the ignition limits of cyanogen – air mixtures vary widely, depending on experimental conditions, e.g., with humid air (1.7% H<sub>2</sub>O); the reported values are 6.4 – 7.25 vol% for the lower limit, and 26.2 – 30.6 vol% for the upper limit.

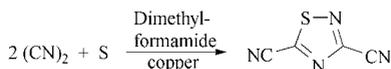
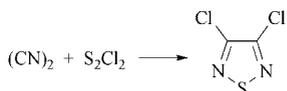
**Chemical Properties.** Cyanogen has a high thermal stability; nevertheless at high temperatures (and when irradiated with UV light), polymerization to paracyanogen occurs [17, 282, 283]. With stoichiometric amounts of air or oxygen, cyanogen burns with the hottest flame (ca. 5000 K) ever observed in chemical reactions [284, 285].

Cyanogen undergoes reactions which depend either on its properties as a pseudohalogen or on the reactivity of the C≡N triple bond [1, 15, 17]:

1. Hydrogenation of cyanogen at 550 – 675 °C gives hydrogen cyanide [286].
2. At 300 – 500 °C, chlorine and cyanogen react to give cyanogen chloride and, subsequently, cyanuric chloride in the presence of an active charcoal catalyst [287, 288].
3. The direct introduction of a cyano group into an aryl or alkyl compound proceeds via a radical- or heat-initiated reaction [289–292].
4. Two moles of hydrogen cyanide add to cyanogen to form diiminosuccinonitrile [293].
5. Cycloadditions (Diels – Alder) with organic dienes give cyanopyridines [294].
6. Alkaline hydrolysis leads to cyanide and cyanate [295].
7. The acid-catalyzed hydrolysis of cyanogen first gives cyanoformamide [296, 297] and then oxamide and oxalic acid. Oxamide [471-46-5] is a nitrogen fertilizer with good depot activity. Its industrial preparation has been

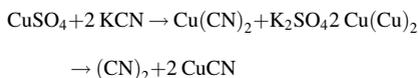
published in several papers; most of the synthetic paths use the isolated  $(\text{CN})_2$  as an intermediate [298–303], but in situ procedures are also known [304].

Heterocyclic compounds are formed by the reaction of cyanogen and disulfur dichloride [305] or sulfur [306]:



## 5.2. Production

Numerous synthetic pathways to cyanogen have been devised [1, 13, 15, 17]. In the laboratory, the compound is normally prepared via cyanide salts; in this case, the reaction of alkali metal cyanides with copper(II) salts is more common than the thermal decomposition of  $\text{Hg}(\text{CN})_2$  or  $\text{AgCN}$  [17].



However, the oxidation of hydrogen cyanide in the presence of a catalyst has greater industrial interest. These reactions are based on the principle of JACQUEMIN [307], that is the conversion of cyanides, by treatment with copper salts, to cyanogen in aqueous solution. In a continuous process, the copper(I) salt formed must be reoxidized rapidly to recycle the catalyst. Reoxidation of copper(I) to copper(II) can be carried out directly with air or oxygen [308, 309] or with  $\text{NO}_2$  [310] the  $\text{NO}$  formed in the second case can then be reoxidized with air or oxygen [311, 312]. The oxidation of hydrogen cyanide to cyanogen in nonaqueous solutions has also been achieved [313, 314]. Hydrogen peroxide is another reoxidation agent [315–318].

The continuous production of  $(\text{CN})_2$  from  $\text{HCN}$  and  $\text{O}_2$  or  $\text{H}_2\text{O}_2$  is utilized industrially on a small scale.

In addition to the liquid-phase oxidation of  $\text{HCN}$ , various gas-phase oxidations have been investigated [319–324].

Cyanogen iodide decomposes to cyanogen and iodine (Chap. 4). In 1984 the reaction of cyanogen halides with trimethylsilyl cyanide in the presence of Lewis acids has been described [325].

Cyanogen prepared by the above procedures contains impurities such as  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{NO}$ ,  $\text{CO}_2$ , or  $\text{ClCN}$ . Its purification can be achieved by fractional vaporization of the crude material [326] or by scrubbing the gas with aqueous  $\text{H}_2\text{O}_2$  [327].

## 5.3. Storage, Transportation, and Uses

**Storage and Transportation.** The flammability and toxicity of cyanogen necessitate special storing and shipping conditions. Cyanogen should be stored in cool, well-ventilated locations, not near to flammable goods or open flames. Dry and pure  $(\text{CN})_2$  can be stored in steel cylinders under pressure and at normal temperatures [328]. Comprehensive studies have been made on the stability of pure cyanogen to heat, pressure, chemical additions, and severe mechanical shock [329]. Shipment must be in accordance with governmental regulations in each country.

**Uses and Economic Value.** Cyanogen is used mainly in the laboratory. In small quantities, cyanogen is used industrially for drug synthesis. The preparation of oxamide (a slow-release fertilizer) has been carried out on a small scale [288]. Large-scale industrial applications are not yet known.

## 6. Toxicology and Occupational Health

**Toxicity and Cyano Compounds.** Hydrogen cyanide and other cyano compounds that can form  $\text{HCN}$  or free cyanide ions are highly toxic to most forms of life. The lethal dose depends on a number of factors, and differs from species to species. A useful survey on this subject can be found in [184]. As shown in this report, the toxicity of metal cyanide complexes is a function of the bond strength between the metal atoms and the cyanide ligands. Toxicity decreases with

**Table 11.** Lethal concentrations of some cyanides (in mg/L)

Substance	Species		
	Fish	<i>Daphnia magna</i>	<i>Escherichia coli</i>
NaCN	0.05 (5 d) [331]	3.4 (48 h) [332]	0.0004 – 0.1 [333]
NaCN	0.3 – 0.7 (96 h) [334]		
NaCN	1.0 (20 months) [335, 336]		
K <sub>3</sub> [Cu (CN) <sub>4</sub> ] [337]	1.0	0.8	2500
CuCN	2.2 [182]		
K <sub>2</sub> [Zn (CN) <sub>4</sub> ] [337]	0.3	13.5	625
Zn (CN) <sub>2</sub>	0.2 – 0.3		
K <sub>2</sub> [Cd (CN) <sub>4</sub> ] [337]	0.75	0.5	250
Cd (CN) <sub>2</sub>	0.17 [182]		
K <sub>2</sub> [Ni (CN) <sub>6</sub> ] [337]	30	75	5000
Na <sub>4</sub> [Fe (CN) <sub>6</sub> ]	500 [182]	> 600 [339]	> 1000 [338]

increasing bond strength, and complexes such as hexacyanocobalt(II) are nontoxic. Hexacyanoferrates(II) and (III) also have very low toxicities [330]. These differences in toxicity are particularly important when the acceptable concentrations of cyanides in wastewater are being considered. Some of the lethal concentrations are shown in Table 11. The LD<sub>50</sub> values of complex hexacyanoferrates (rat, oral) are as follows:

Ca <sub>2</sub> [Fe (CN) <sub>6</sub> ] · 11 H <sub>2</sub> O	> 5110 mg/kg
Na <sub>4</sub> [Fe (CN) <sub>6</sub> ] · 10 H <sub>2</sub> O	> 5110 mg/kg
K <sub>4</sub> [Fe (CN) <sub>6</sub> ] · 3 H <sub>2</sub> O	3613 mg/kg
K <sub>3</sub> [Fe (CN) <sub>6</sub> ]	3503 mg/kg

**Poisoning by Hydrogen Cyanide and Alkali Metal Cyanides.** Hydrogen cyanide is easily absorbed, even through intact skin and mucous membranes. Not even full respiratory protection can prevent hydrogen cyanide from penetrating into the organism. The speed of absorption of orally ingested cyanide depends on the contents of the stomach and gastric pH; empty stomach and low pH lead to rapid absorption of cyanide. Symptoms [340] of the poisoning may vary somewhat, depending on the quantity of hydrogen cyanide absorbed or the quantity of cyanide ingested. Low concentrations of hydrogen cyanide irritate the nasopharyngeal cavity; occasional complaints involve headache, anxiety, and nausea. Rapid inhalation of the lethal dose (ca. 50 – 100 mg) of hydrogen cyanide results in collapse of the individual. This apoplectic form syndrome, characterized by a short spasmodic stage with subsequent respiratory paralysis,

results in immediate death. Poisoning symptoms following oral ingestion of cyanides, on the other hand, exhibit a slow progress, even with large doses (150 – 250 mg), because of the slow release of hydrogen cyanide. Case histories described in the literature involve poisoning durations up to several hours. Cyanide affects many enzymes. The inhibition of cytochrome c oxidase is responsible for the acute effects and the marked metabolic changes (lactic acidosis). As in other intoxication, treatment includes the support of vital signs (supportive therapy), prevention of further poison absorption, and enhancement of poison elimination. The administration of antidotes in severe cyanide poisoning is mandatory, although this opinion has been contradicted.

The following concentrations of hydrogen cyanide and other cyanides in air are considered acceptable at the workplace:

TLV-TWA	(hydrogen cyanide)	10 mg/m <sup>3</sup> [341]
MAK	(hydrogen cyanide)	11 mg/m <sup>3</sup> [342]
TLV-TWA	(cyanide dust, as CN)	5 mg/m <sup>3</sup> [341]
MAK	(cyanide dust, as CN)	5 mg/m <sup>3</sup> [342]

**Therapy for Poisoning by Hydrogen Cyanide and Other Cyanides.** Different antidotes or combination of antidotes are preferred in different countries. The mechanisms of antidotal action follow different principles:

1. Direct complexation of the cyanide and excretion as cyanide – antidote complex (hydroxocobalamin, dicobalt edetate)
2. Methemoglobin-forming compounds which shift the cyanide from the intracellular to the

blood compartment [amyl nitrite, sodium nitrite, 4-dimethylaminophenol (4-DMAP)]

3. Sulfate donors, which enhance the natural pathway of detoxification (thiosulfate).

The first aid given to victims of hydrogen cyanide poisoning is not fundamentally different from the measures taken in other acute emergencies. The success of the treatment, however, depends on the immediate start of antidote therapy. Seconds may determine the success or failure of the treatment of cyanide poisoning. The therapeutic measures required depend on the particular poisoning syndrome encountered. The initial treatment is of supreme importance and must be aimed at safeguarding vital functions such as respiration and circulation.

### Cyanogen Chloride, Cyanogen Bromide

[340]. Because of their high volatility, cyanogen chloride and cyanogen bromide are strong irritants to mucous membranes (eyes, lungs). Their effects are essentially identical to those produced by hydrogen cyanide; however, they are rarely encountered because the irritating effects serve as a warning of potential danger. When handling liquid cyanogen chloride, attention must be paid to the potential for skin absorption. The exposure limit of cyanogen chloride (TLV – TWA) is  $0.6 \text{ mg/m}^3$  [341]. The therapy is analogous to that for hydrogen cyanide poisoning.

**Cyanogen** [340]. Cyanogen irritates mucous membranes and is probably hydrolyzed in the organism to hydrogen cyanide and cyanic acid. The symptoms are similar to those produced by hydrogen cyanide poisoning.

TLV – TWA	$20 \text{ mg/m}^3$ [341]
MAK	$22 \text{ mg/m}^3$ [342]

The therapy is analogous to that for hydrogen cyanide poisoning.

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