

MERCURY

1. Introduction

Mercury [7439-97-6], Hg, atomic number 80, atomic weight 200.59, also called quicksilver, is a heavy, odorless metal belonging to Group 12 (IIB) of the Periodic Table. Elemental mercury is a liquid at room temperature, having a characteristic bright, silvery appearance. The symbol Hg is taken from the Latin word *hydrargyrum*, meaning liquid silver. Unlike the other two Group 12 elements, mercury exhibits two valences, mercurous, Hg^+ , and mercuric, Hg^{2+} . Samples of mercury have been found in graves dating to the fifteenth or sixteenth century BC, where cinnabar [19122-79-3], HgS , was used as a pigment for cave and body decoration.

The first recorded mention of mercury metal was by Aristotle in the fourth century BC, at a time when it was used in religious ceremonies. By the time of Pliny, mercury was a familiar substance, and its preparation by roasting cinnabar was well known. The ancient Egyptians, Greeks, and Romans used mercury for cosmetic and medical preparations, and for amalgamation. Although it resembles a metal, mercury's liquid nature usually caused it to be classified among the "waters." It was not until sometime in the period 500–700 AD that mercury was accepted as a metal, and the astrological symbol that had been assigned to tin was given to mercury. The ability of mercury to impart a silvery color to other metals also gave it a special position among the alchemists (1).

In the late fifteenth century AD mercury was successfully used as a treatment for syphilis. In the late sixteenth century the development of the Patio process for the recovery of silver by amalgamation (see SILVER AND SILVER ALLOYS) greatly increased the consumption of mercury. Usage of mercury increased in 1643 when Torricelli invented the barometer, and again in 1720 when Fahrenheit invented the mercury thermometer. Other scientific and medical applications followed. Industrial usage after 1900, particularly in electrical applications, expanded rapidly, offsetting the sharp decline in its use in amalgamation.

Applications of mercury include use in batteries (qv), chlorine and caustic soda manufacture (see ALKALI AND CHLORINE PRODUCTS), pigments (see PIGMENTS, INORGANIC), light switches, electric lighting, thermostats, dental repair (see DENTAL MATERIALS), and preservative formulations for paints (qv) (1–3). As of the end of the twentieth century, however, increased awareness of and concern for mercury toxicity has resulted in both voluntary and regulatory reduction of mercury usage (see also MERCURY COMPOUNDS).

2. Occurrence

Mercury metal is widely distributed in nature, usually in quite low concentrations. The terrestrial abundance is on the order of 50 parts per billion (ppb), except in mercuriferous belts and anthropogenically contaminated areas. In soils, the average mercury content is about 100 ppb, ranging from 30 to 500 ppb. In rocks, mercury content ranges from 10 to 20,000 ppb. Surface waters, except where special geological conditions prevail or where anthropogenic

sources occur, generally contain less than 0.1 ppb total mercury. The average mercury content of sea waters has been found to range from 0.1 to 1.2 ppb (2). The most important mineral of mercury is cinnabar, found in rocks near recent volcanic activity or hot spring areas and in mineral veins or fractures as impregnations (2–4). In addition to cinnabar, corderoite [53237-82-4], $\text{Hg}_3\text{S}_2\text{Cl}_2$; livingstonite [12532-29-5], HgSb_4S_8 ; montroydite [24401-75-0], HgO ; terlinguaite [12394-37-5], Hg_2OCl ; calomel [10112-91-1], HgCl ; and metacinnabar [23333-45-1], a black form of cinnabar, are commonly found in mercury deposits (5). The numerous other mercury minerals are rare and not commercially significant.

Mercury ore deposits occur in faulted and fractured rocks, such as limestone, calcareous shales, sandstones, serpentine, chert, andesite, basalt, and rhyolite. Deposits are mostly epithermal in character, ie, minerals were deposited by rising warm solutions at comparatively shallow depths from 1–1000 m (6).

3. Properties

Mercury has a uniform volume expansion over its entire liquid range (see Table 1). This, in conjunction with high surface tension, ie, inability to wet and cling to glass, makes mercury extremely useful for barometers, manometers, thermometers, and many other measuring devices. Mercury also has a propensity to form alloys (amalgams) with almost all other metals except iron, and at high temperatures, even with iron. Because of low electrical resistivity, mercury is rated as one of the best electrical conductors among the metals. Mercury has a high thermal neutron-capture cross section ($360 \times 10^{-28} \text{ m}^2$ (360 barns)), enabling it to absorb neutrons and act as a shield for atomic devices. Its high thermal conductivity also permits it to act as a coolant. The physical and chemical properties of mercury are given in Table 1, and the distribution of the stable isotopes in Table 2. A number of artificial isotopes also are known (see RADIOISOTOPES).

The volume expansion, V_t , of mercury may be calculated over its entire liquid range by

$$V_t = V_0(1 + 0.18182 \times 10^{-3} t + 0.0078 \times 10^{-6} t^2)$$

where V_0 is the known volume of mercury at a given temperature, t , in $^{\circ}\text{C}$.

The specific heat varies with temperature. For solid mercury it increases but in liquid mercury it drops such that the specific heat at 210°C is the same as that at -75°C (Table 3). Up to 50°C , specific heat in J/g is given by the formula $0.1418 - 0.0004343(t + 36.7)$ for temperatures t in $^{\circ}\text{C}$; from 50 – 150°C , the formula should be modified by an additional corrective factor of $-0.000025(t - 50)$; and between 150 and 250°C , $-0.0000126(t - 150)$. Values for temperatures above 150°C are not as accurate as those for lower temperatures.

The vapor pressure of mercury, P , also behaves irregularly but may be obtained for temperatures from 0–150 °C by the following:

$$\log P = (-3212.5/T) + 7.150$$

and from 150°–400°C by

$$\log P = (-3141.33/T) + 7.879 - 0.00019 t$$

where P is in kPa (101.3 kPa = 760 mm Hg), T is the absolute temperature in K, and t is the temperature in °C. The accuracy of these formulas is believed to be within 1%.

Another valuable property of mercury is its relatively high surface tension, 480.3 mN/m(= dyn/cm) at 0 °C, as compared to 75.6 mN/m for water. Because of its high surface tension, mercury does not wet glass and exhibits a reverse meniscus in a capillary tube.

Electrode reduction potentials of mercury are given in Table 4.

At ordinary temperatures, mercury is stable and does not react with air, ammonia (qv), carbon dioxide (qv), nitrous oxide, or oxygen (qv). It combines readily with the halogens and sulfur, but is little affected by hydrochloric acid, and is attacked only by concentrated sulfuric acid. Both dilute and concentrated nitric acid dissolve mercury, forming mercurous salts when the mercury is in excess or no heat is used, and mercuric salts when excess acid is present or heat is used. Mercury reacts with hydrogen sulfide in the air and thus should always be covered.

The only metals having good or excellent resistance to corrosion by amalgamation with mercury are vanadium, iron, niobium, molybdenum, cesium, tantalum, and tungsten (8). The diffusion rates of some metals in mercury are given in Table 5.

4. Production and Shipment

4.1. Primary Production. Mercury ore is mined by both surface and underground methods. The latter furnishes about 90% of the world's production. Mercury is recovered also as a by-product in the mining and processing of precious and base metals (see MINERAL RECOVERY AND PROCESSING). Small quantities of mercury have been produced by processing ground under and adjacent to the sites of less efficient ore-burning furnaces used in earlier-day mercury recovery operations. Mercury is also produced by working mine dumps and tailing piles, particularly those accumulated during turn-of-the-century mining operations. The average grade of mercury ore mined from large mines throughout the world in the latter part of the twentieth century has ranged from 4 to 20 kg/t. Total recovery has approached 95%. The average grade of ore has generally declined as a result of the practice of mining the richest parts of ore bodies to realize a higher profit and because prices have generally increased, allowing lower grade ores to be exploited. Since 1990, the only mine production of mercury

in the United States has come as a by-product of gold mining operations (14) (see GOLD AND GOLD COMPOUNDS).

4.2. Secondary Production. Smaller quantities of mercury are produced each year from industrial scrap and waste materials, such as discarded dental amalgams, batteries, lamps, switches, measuring devices, control instruments, and wastes and sludges generated in laboratories and electrolytic refining plants (3). Mercury in these materials may be recovered *in situ* or by firms specializing in secondary recovery (see RECYCLING). Traditionally, secondary production has depended on the price of mercury. Secondary production of mercury in the United States has increased steadily in the 1990s, however, as a result of the rising costs of hazardous waste disposal and increased restrictions on mercury disposal.

4.3. Shipping. Prime virgin-grade mercury is packaged in wrought iron or steel flasks containing 34.5 kg of the metal. Mercury of greater purity, produced by multiple distillation or other means, may be marketed in flasks but is usually packaged in small glass or plastic containers.

5. Processing

5.1. Primary. Mercury metal is produced from its ores by standard methods throughout the world. The ore is heated in retorts or furnaces to liberate the metal as vapor which is cooled in a condensing system to form mercury metal (9). Retorts are inexpensive installations for batch-treating concentrates and soot. These require only simple firing and condensing equipment. For larger operations, either continuous rotary kilns or multiple-hearth furnaces with mechanical feeding and discharging devices are preferred. Using careful control at properly designed plants, 95% or more of the mercury in the ore can be recovered as commercial-grade (99.9% purity) mercury.

Other recovery methods have been used (10). These include leaching ores and concentrates using sodium sulfide [1313-82-2] and sodium hydroxide [1310-73-2], and subsequently precipitating with aluminum [7429-90-5], or by electrolysis (11). In another process, the mercury in the ore is dissolved by a sodium hypochlorite [7681-52-9] solution, the mercury-laden solution is then passed through activated carbon [7440-44-0] to absorb the mercury, and the activated carbon heated to produce mercury metal. Mercury can be extracted from cinnabar by electrooxidation (12,13).

5.2. Secondary. Scrap material, industrial and municipal wastes, and sludges containing mercury are treated in much the same manner as ores to recover mercury. Scrap products are first broken down to liberate metallic mercury or its compounds. Heating in retorts vaporizes the mercury, which upon cooling condenses to high purity mercury metal. Industrial and municipal sludges and wastes may be treated chemically before roasting.

6. Economic Aspects

Mercury toxicity from environmental pollution and occupational exposure has become an area of concern throughout the world. Since the 1980s much effort has been devoted both in terms of legislation and voluntary action, to limiting the production and use of mercury, and to finding technologies designed to supplant the need for mercury. As a result, overall demand for mercury has decreased throughout the industrialized world. Table 6 gives a breakdown by country of worldwide mercury production.

Spain, which until 1989 was the world's largest producer of mercury, ceased mine production after 1990, although 100 t of mercury were produced in 1991 from stockpiled materials. China, Mexico, and Russia were the largest producers in 1992 (14).

The last operating mercury mine in the United States closed in November of 1990. Since 1990, the only mine production of mercury in the United States has come as a by-product of gold-mining operations. Mercury occurs with most gold ores and must be recovered to avoid release into the environment (14). Secondary production of mercury in the United States has been increasing as a result of the growing cost restrictions on the disposal of mercury-containing wastes (3,14). U.S. imports and exports have also increased since 1989 (14). In the early 1990s over 50% of the exported U.S. mercury went to the Netherlands including 700 t in 1992 (14).

The U.S. Defense Logistics Agency (DLA), which maintains the U.S. National Defense Stockpile (NDS), sold 267 t of stockpiled mercury in 1992 (14). The DLA also sold 103 t of secondary mercury from the Department of Energy (DOE) stocks at Oak Ridge, Tennessee. The DLA accepts bids for prime virgin mercury on a daily basis, and for secondary mercury once a month. Inventories on December 31, 1992 were 4766 t of mercury in the NDS and 121 t of DOE mercury (14). The goal for both is zero.

Production and use of mercury is expected to continue to decrease, owing to mercury toxicity. Many of the traditional uses have either declined or have been eliminated (14).

7. Grades, Specifications, and Quality Control

The commercial-grade (99.9%) purity marketed as prime virgin-grade mercury has a clean bright appearance and contains less than 1 ppm of dissolved base metals. Prime virgin-grade mercury of lower purity is brought up to specification by filtration, redistillation, or electrolytic processing.

Triple-distilled mercury is of highest purity, commanding premium prices. It is produced from primary and secondary mercury by numerous methods, including mechanical filtering, chemical and air oxidation of impurities, drying (qv), electrolysis, and most commonly multiple distillation.

The purity of mercury can be estimated by its appearance. Because mercury has such a high specific gravity, almost all impurities, including amalgams, are

lighter and float on the surface, causing the bright, mirror-like surface to become dull and black. The coating of oxides of base metal is called film or scum and a clean, bright appearance usually signifies an impurity content of <5 ppm (15,16). Other tests measure the residue remaining after the mercury is evaporated (17,18).

8. Analytical Methods

8.1. Ore. The assay of mercury ores is not simple, owing to the difficulties encountered in obtaining representative ore samples. Crystalline cinnabar is extremely brittle causing it to break loose from adjacent rock and fall into the sample being collected. This uncontrollable salting of the sample can give results as much as several hundred percent over the actual mercury content of the sample.

The two assay methods preferred employ distillation–amalgamation or distillation–titration techniques. In the former, the weighted sample is heated with a flux such as iron [7439-89-6] filings to volatilize the mercury, which is then amalgamated with silver [7440-22-4] or gold [7440-57-5] foil. The mercury content is calculated from the change in foil weight. In the titration method, the sample is heated and the mercury volatilized and collected as metal, which is then dissolved in hot nitric acid. Potassium permanganate [7722-64-7] is added to oxidize the mercury and a peroxide to destroy excess permanganate. After ferric sulfate [10028-22-5], a nitrate indicator, is added to the solution, it is then titrated with standard potassium thiocyanate [333-20-0] solution to a faint pink end point. When a 0.5-g sample is titrated with a 1/400-*N* solution, each milliliter of titrating solution is equivalent to 0.41 kg/t of mercury.

8.2. Commercial Product. The efficiency of furnace and condensation operations can be checked by spot-testing the condensed mercury for precious and base metal content, the most common contaminants from mining operations. Gold is determined by dissolving a 10-g sample of mercury in equal parts of distilled water and 15-*N* nitric acid. The residue is evaporated with aqua regia [8007-56-5]. If no precipitate results using sodium hydroxide and hydrogen peroxide [7722-84-1], no gold is present. Silver content is determined by spot-testing using trivalent manganese reagent. Base metals are determined by dissolving the sample in concentrated hydrochloric acid, volatilizing the mercuric chloride [7847-94-7], and analyzing the residue gravimetrically.

Ultrapure (triple distilled) mercury is commonly tested by evaporation or spectrographic analysis. In the former, a composite sample is evaporated and the residue weighed. In spectrographic analysis, a sample is dissolved and evaporated, the residue mixed with graphite [7782-42-5], and the emission spectrum determined with a spectrograph.

8.3. Trace Mercury. There are a number and variety of methods and instruments to determine trace quantities of both inorganic and organic mercury in natural or synthetic substances (19) (see also TRACE AND RESIDUE ANALYSIS). Literature describing numerous techniques and trace element analysis of a myriad of mercury-containing substances is available (20). Only the most commonly used methods are mentioned herein.

Atomic Absorption Spectroscopy. Mercury, separated from a measured sample, may be passed as vapor into a closed system between an ultraviolet lamp and a photocell detector or into the light path of an atomic absorption spectrometer. Ground-state atoms in the vapor attenuate the light decreasing the current output of the photocell in an amount proportional to the concentration of the mercury. The light absorption can be measured at 253.7 nm and compared to established calibrated standards (21). A mercury concentration of 0.1 ppb can be measured by atomic absorption.

Neutron Activation Analysis. A measured sample activated by neutron bombardment emits gamma rays that are used to determine the mercury content by proton-spectrum scanning. Mercury concentrations as low as 0.05 ppb have been determined by this method.

X-Ray Methods. In x-ray fluorescence the sample containing mercury is exposed to a high intensity x-ray beam which causes the mercury and other elements in the sample to emit characteristic x-rays. The intensity of the emitted beam is directly proportional to the elemental concentration in the sample (22). Mercury content below 1 ppm can be detected by this method. X-ray diffraction analysis is ordinarily used for the qualitative but not the quantitative determination of mercury.

Colorimetric Method. A finely powdered sample treated with sulfuric acid, hydrobromic acid [10035-10-6], and bromine [7726-95-6] gives a solution that when adjusted to pH 4 may be treated with dithizone [60-10-6] in *n*-hexane [110-54-3] to form mercuric dithizonate [14783-59-6] (20). The resultant amber-colored solution has a color intensity that can be compared against that of standard solutions to determine the mercury concentration of the sample. Concentrations below 0.02 ppm have been measured by this method.

9. Mercury in the Environment

9.1. Releases. Global releases of mercury into the environment may be either natural or anthropogenic. Natural mercury sources are mainly from volcanoes and volatilization from waters, soils, flora, and fauna (3); anthropogenic releases result principally from the production of metals and combustion of coal (qv), municipal refuse, sewage sludge, and wood (qv). Annual global releases of mercury into the atmosphere from natural sources have been estimated to be on the order of 2700–6000 t; annual anthropogenic releases of mercury into the atmosphere have been reported from 630–6800 t (23,24). Hence, natural and anthropogenic releases of mercury into the atmosphere are roughly equivalent.

Global anthropogenic releases of mercury into the biosphere are approximately 11,000 metric tons per year (24). The release of mercury into aquatic ecosystems results from electricity production, manufacturing processes, domestic wastewater and sewage sludge, mining, and fallout of atmospheric mercury (see METALLURGY, EXTRACTIVE; WASTES, INDUSTRIAL). The release of mercury into soils results from mining and smelting activities, coal fly ash and bottom ash, wood wastes, commercial wastes, sewage sludge, urban refuse, fallout of atmospheric mercury, and other sources (3).

Chlor-alkali production is the largest industrial source of mercury release in the United States (see ALKALI AND CHLORINE PRODUCTS). For the 1991 reporting year, chlor-alkali facilities accounted for almost 20% of the facilities that reported releases of mercury to the U.S. Environmental Protection Agency (EPA) for inclusion onto the Toxics Release Inventory (TRI)(25).

9.2. Regulations. In order to decrease the amount of anthropogenic release of mercury in the United States, the EPA has limited both use and disposal of mercury. In 1992, the EPA banned land disposal of high mercury content wastes generated from the electrolytic production of chlorine-caustic soda (14), accompanied by a one-year variance owing to a lack of available waste treatment facilities in the United States. A thermal treatment process meeting EPA standards for these wastes was developed by 1993. The use of mercury and mercury compounds as biocides in agricultural products and paints has also been banned by the EPA.

The State of New Jersey has passed a law restricting the sale and disposal of batteries (qv) containing mercury, requiring manufacturers to reduce the mercury content of each battery to 1 ppm by weight by 1995, and to establish a collection program for spent batteries (14). Another New Jersey law bans the sale of products having cadmium, mercury, or other toxic materials in the packaging (14) (see CADMIUM AND CADMIUM ALLOYS; CADMIUM COMPOUNDS; MERCURY COMPOUNDS).

California and Minnesota have placed restrictions on the disposal of fluorescent light tubes, which contain from 40–50 mg of mercury per tube, depending on size. After batteries, fluorescent lamps are the second largest contributor of mercury in solid waste streams in the United States (3,14). A California law classifies the disposal of 25 or more fluorescent lamp tubes as hazardous waste. In Minnesota, all waste lamps generated from commercial sources are considered hazardous waste. Private homes are, however, exempt from the law (14). Other states have proposed similar regulations. Several companies have developed technologies for recovering mercury from spent lamps (14).

A goal of reducing total mercury releases in the United States by 33% between 1988 to 1992, and 50% by 1995 was set by the EPA. The 1992 goal was more than achieved: United States reportable mercury releases were reduced by 39% by 1991 (26). In the United States, discards of mercury in municipal solid waste streams were approximately 643 t in 1989 (3). As a result of increased restrictions on the use and disposal of mercury, by the year 2000 mercury in municipal solid waste streams is expected to be about 160 t (3).

10. Health and Safety Factors

10.1. Exposure. The exposure of humans and animals to mercury from the general environment occurs mainly by inhalation and ingestion of terrestrial and aquatic food chain items. Fish generally rank the highest (10–300 ng/g) in food chain concentrations of mercury. Swordfish and pike may frequently exceed 1 µg/g (27). Most of the mercury in fish is methyl mercury [593-74-8]. Worldwide, the estimated average intake of total dietary mercury is 5–10 µg/d in Europe, Russia, and Canada, 20 µg/d in the United States, and 40–80 µg/d in Japan (27).

In occupational settings mercury exposure results predominantly from direct dermal contact or inhalation of mercury vapors (27). Chlor-alkali plants are one of the principal sources for occupational exposure to mercury (28,29). Mining and refining of mercury contribute to exposure, and the processing of cinnabar can result in high exposures to the skin and lungs, producing poisoning in a relatively short time. Exposure also occurs in the manufacture and use of mercury-containing instruments through breakage, spilling, or carelessness. Dentists and dental assistants can be exposed to significant quantities of mercury during the preparation and use of mercury amalgam (30) (see DENTAL MATERIALS). People who have mercury amalgam dental restorations may be exposed to 1–2 $\mu\text{g}/\text{d}$ of mercury as a result of its dissolution in saliva. Exposure to mercury from amalgam restorations, however, is considered unlikely to pose a health risk to the patient(30).

Recommended safety measures which minimize occupational exposure to mercury include the use of efficient respirators, adequate ventilation and air-exhaust systems, employee warning signs and messages, training in accident emergency procedures, immediate and thorough cleanup of spills, airtight storage of mercury-containing wastes, and frequent monitoring of mercury levels in the work area. Additional precautions include coverall-type work clothes, maintenance of floors, work surfaces, and equipment such that crevices that might hold spilled mercury are not present, and adequate washing facilities and provision for showering at the end of the work period. Medical and dental examination at frequent intervals is also recommended.

10.2. Toxicity. The toxic effects of mercury and mercury compounds (qv) are well known, and several detailed discussions on mercury toxicity are available (31–35). The propensity of mercury to accumulate in the food chain has resulted in many outbreaks of mercury toxicity in humans throughout the world. Elemental mercury is not particularly toxic when ingested, owing to very low levels of absorption from the gastrointestinal tract. Inhaled mercury vapor, however, undergoes complete absorption by the lung and is then oxidized to the divalent mercuric cation, Hg^{2+} , by catalase enzymes in erythrocytes (31). Within a few hours the deposition of inhaled mercury vapor resembles that which occurs after ingestion of mercuric salts, but with one important difference. Because mercury vapor crosses membranes much more rapidly than does divalent mercury, a significant amount of the vapor enters the brain before it is oxidized. Therefore, toxicity to the central nervous system is more prominent after exposure to mercury vapor than to divalent mercury (31–35).

Short-term exposure to mercury vapor may produce symptoms within several hours. These symptoms include weakness, chills, metallic taste, nausea, vomiting, diarrhea, labored breathing, cough, and a feeling of tightness in the chest. Pulmonary toxicity may progress to an interstitial inflammation of the lung with severe compromise of respiratory function. Recovery, although usually complete, may be complicated by residual interstitial growth of unnecessary fibrous tissue (31).

Chronic exposure to mercury vapor produces an insidious form of toxicity that is manifested by neurological effects and is referred to as the asthenic vegetative syndrome (31). The syndrome is characterized by tremor, psychological depression, irritability, excessive shyness, insomnia, emotional instability,

forgetfulness, confusion, and vasomotor disturbances such as excessive perspiration and uncontrolled blushing (31,32). Common features of chronic mercury vapor intoxication are severe salivation and gingivitis (31). In fact, the triad of increased excitability, tremors, and gingivitis has been recognized historically as the primary manifestations of exposure to mercury vapor when mercuric nitrate [7783-34-8] was used in the fur, felt, and hat industries (31). Renal dysfunction has also been reported to result from long-term industrial exposure to mercury vapor (31–33).

The biochemical basis for the toxicity of mercury and mercury compounds results from its ability to form covalent bonds readily with sulfur. Prior to reaction with sulfur, however, the mercury must be metabolized to the divalent cation. When the sulfur is in the form of a sulfhydryl (—SH) group, divalent mercury replaces the hydrogen atom to form mercaptides, X—Hg—SR and Hg(SR)_2 , where X is an electronegative radical and R is protein (36). Sulfhydryl compounds are called mercaptans because of their ability to capture mercury. Even in low concentrations divalent mercury is capable of inactivating sulfhydryl enzymes and thus causes interference with cellular metabolism and function (31–34). Mercury also combines with other ligands of physiological importance such as phosphoryl, carboxyl, amide, and amine groups. It is unclear whether these latter interactions contribute to its toxicity (31,36).

The affinity of mercury for thiols provides the basis for treatment of mercury poisoning using chelating agents (qv) such as dimercaprol [59-52-9], for high level exposures or symptomatic patients, or penicillamine [52-67-5], for low level exposures or asymptomatic patients (32). Dimercaprol (a dithiol) reacts more readily with mercury than do monothiols such as cysteine [52-90-4], but dimercaprol does not easily form a ring complex with mercury, because the bond angle of divalent mercury is 180° (36). Detailed discussions on the treatment of mercury poisoning are available (31,32). Removal of the patient from the source of mercury exposure and measurement of the concentration of mercury in the blood should be accomplished as quickly as possible.

11. Uses

Mercury consumption in the United States is summarized through 1992 in Table 7. Overall worldwide consumption of mercury declined in the 1980s and early 1990s. A detailed discussion of the uses and applications of mercury is available (3).

11.1. Electrolytic Preparation of Chlorine and Caustic Soda. The preparation of chlorine [7782-50-5] and caustic soda [1310-73-2] is an important use for mercury metal. Since 1989, chlor-alkali production has been responsible for the largest use for mercury in the United States. In this process, mercury is used as a flowing cathode in an electrolytic cell into which a sodium chloride [7647-14-5] solution (brine) is introduced. This brine is then subjected to an electric current, and the aqueous solution of sodium chloride flows between the anode and the mercury, releasing chlorine gas at the anode. The sodium ions form an amalgam with the mercury cathode. Water is added to the amalgam to remove the sodium [7440-23-5], forming hydrogen [1333-74-0] and sodium

hydroxide and relatively pure mercury metal, which is recycled into the cell (see ALKALI AND CHLORINE PRODUCTS).

11.2. Batteries. Many batteries intended for household use contain mercury or mercury compounds. In the form of red mercuric oxide [21908-53-2], mercury is the cathode material in the mercury–cadmium, mercury–indium–bismuth, and mercury–zinc batteries. In all other mercury batteries, the mercury is amalgamated with the zinc [7440-66-6] anode to deter corrosion and inhibit hydrogen build-up that can cause cell rupture and fire. Discarded batteries represent a primary source of mercury for release into the environment. This industry has been under intense pressure to reduce the amounts of mercury in batteries. Although battery sales have increased greatly, the battery industry has announced that reduction in mercury content of batteries has been made and further reductions are expected (3). In fact, by 1992, the battery industry had lowered the mercury content of batteries to 0.025 wt% (3). Use of mercury in film pack batteries for instant cameras was reportedly discontinued in 1988 (3).

11.3. Electric Lighting. Mercury is used in several types of electric lamps (light bulbs). Mercury-containing lamps include fluorescent lamps and high intensity discharge (HID) lamps such as mercury vapor, metal halide, and high pressure sodium lamps. Applications include street lighting, industrial and office lighting, floodlighting, photography, underwater lighting, insect lamps, and sun lamps (3). Fluorescent mercury content varies with both bulb size and wattage. Lamp redesign and improvements in manufacturing process control have reduced mercury content by approximately 25%. The average mercury content in fluorescent and HID lamps as of 1992 was estimated to be 55 and 25 mg, respectively (3).

11.4. Electric Light Switches and Thermostats. Mercury electric light switches have been manufactured since the 1960s. Less than one million mercury switches are produced each year, and are in decline (3). Mercury switches may be used wherever lighting is used. The mercury is inside a metal encapsulation. Mercury thermostats have been used for many years. Since the early 1980s, however, mercury thermostats have begun to be replaced by programmable electronic thermostats, which do not contain mercury. The nonmercury, programmable devices are substantially higher in cost.

11.5. Dentistry. Mercury is used in dental amalgams for fillings in teeth (see DENTAL MATERIALS). Dental uses have accounted for 2–4% of total U.S. mercury consumption since 1980 and generally 3–6% before that time (3). Dental amalgams used to fill cavities in teeth are approximately 50% mercury by weight. Dental use of mercury can be expected to continue to decrease, in part because of more effective cavity prevention as well as development and increasing use of alternative dental materials such as plastics and ceramics, and increasing awareness of the environmental and health effects of mercury.

11.6. Industrial and Control Instruments. Mercury is used in many industrial and medical instruments to measure or control reactions and equipment functions, including thermometers, manometers (flow meters), barometers and other pressure-sensing devices, gauges, valves, seals, and navigational devices (see PRESSURE MEASUREMENTS; PROCESS CONTROL; TEMPERATURE MEASUREMENT). Whereas mercury fever thermometers are being replaced by digital thermometers, most

fever thermometers in residential use are expected to continue to contain mercury because of the higher cost of digital thermometers and the relatively infrequent home use of fever thermometers.

11.7. Pigments. Mercury has a long history of use in the pigment industry (see PIGMENTS). Mercury sulfide [1344-48-5], in the form of cinnabar ore, has been used as a colorant since antiquity. Most of the mercury in pigments is used in plastics, often in combination with cadmium. There are strong pressures to reduce or eliminate all heavy metals from pigments, and the use of mercury in pigments has been declining steadily. Production of mercury-containing pigments in the United States was discontinued in 1988, but it is likely that some mercury pigments are imported into the United States (3). Production of mercury-containing pigments outside of the United States is also expected to decline (3).

11.8. Catalysts. Mercury is or has been used in the catalysis (qv) of various plastics, including polyurethane [26778-67-6], poly(vinyl chloride) [9002-86-2], and poly(vinyl acetate) [9003-20-7]. Most poly(vinyl chloride) and poly(vinyl acetate) is manufactured by processes that do not use mercury (3).

11.9. Explosives. Mercury, in the form of organic complexes, eg, mercury fulminate [628-86-4], has had long usage in explosives (see EXPLOSIVES AND PROPELLANTS). In the United States all mercury for use in explosives is diverted to military uses. An explosive based on mercuric 5-nitrotetrazole [60345-95-1] has been developed, but its use is on a small scale and in research and development only (3).

11.10. Special Paper Coating. Mercury bromide [10031-18-2] and mercury acetic acid [1600-27-7] are used in the coating of a specialized paper and film (see PAPER; MEDICAL IMAGING TECHNOLOGY). The coating, which also contains silver, is applied to paper that is used when scanning off of a cathode ray tube. A very high resolution is obtained from the process. This type of printing occurs in hospitals and newspaper publishing, and is utilized in microfiche printers. By 1995 mercury is expected to be eliminated entirely from this application (3).

11.11. Pharmaceuticals. A variety of mercury compounds have had pharmaceutical applications over the years, eg, mercury-containing diuretics and antiseptics. Whereas some mercury compounds remain available for use as antiseptics such as merbromin [129-16-8], mercuric oxide, and ammoniated mercury [10124-48-8], or as preservatives such as thimerosal [54-64-8] in drugs and cosmetics, most have been supplanted by more effective substances. A detailed discussion of mercury-containing antiseptics is available (37). Many hospitals use mercury metal to serve as weight for keeping nasogastric tubes in place within the stomach.

11.12. Discontinued Uses. Agricultural Products. Mercury and mercury compounds were at one time used extensively as seed disinfectants (see FUNGICIDES, AGRICULTURAL). In the United States, these uses were greatly restricted by the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA). In 1978, FIFRA was amended such that the only acceptable uses for mercury under FIFRA are for treatment of outdoor textiles, and to control brown mold on freshly sawn lumber, Dutch elm disease, and snow mold. Although allowable under FIFRA, it is doubtful whether mercury compounds are used for these

purposes. No use of mercury or mercury compounds is permitted on food crops in the United States (3). Additional amendments to FIFRA have prohibited the importation of foodstuffs containing residues of banned pesticides. Also, the U.S. government in turn is required to notify foreign countries of health hazards before allowing the export of canceled or restricted pesticides (3).

Paints. For many years mercury-based biocides such as phenylmercuric acetate [62-38-4], 3-(chloromethoxy)propylmercuric acetate, di(phenylmercury) dodeceny succinate [27236-65-3], and phenylmercuric oleate [104-60-9], were registered as biocides in interior and exterior paints, and in antifouling paints (see PAINT). In 1972 the use of mercury in antifouling paint formulations was banned. As of July 1990, most registrations for mercury biocides used in interior and exterior paints and coatings (qv) were voluntarily canceled by the registrants (3). In 1991, EPA announced the voluntary cancellation of the remaining mercury biocide registrations (3). No mercury is allowed in the manufacture of paints in the United States.

Other Uses. Other uses of mercury that have been discontinued include coatings for mirrors, manufacture of certain types of glass, treatment of felt, and as a fungicide in paper.

This article has been reviewed by the Office of Pollution Prevention and Toxics, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Agency, nor does mention of commercial products constitute endorsement or recommendation for use.

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Table 1. Physical and Chemical Properties of Mercury^a

Property	Value
accommodation coefficient, at -30 to 60 °C, $(T_3 - T_1)/(T_2 - T_1)^b$	1.00
angle of contact of glass at 18 °C, deg	128
atomic distance, nm	0.30
melting point, °C	-38.87
boiling point, °C	356.9
triple point, °C	-38.84168
bp rise with pressure, °C/kPa ^c	0.5595
compressibility (volume) at 20 °C, MPa ^{-1d}	39.5×10^{-6}
condensation on glass, °C	-130 to -140
conductivity, thermal, W/(cm ² ·K)	0.092
critical density, g/cm ³	3.56
critical pressure, MPa ^d	74.2
critical temperature, °C	1677
crystal system	rhombohedral
density, g/cm ³ at melting point	14.43
-38.8 °C (solid)	14.193
0 °C	13.595
20 °C	13.546
emf, of hot Hg at 100 °C, mV ^e	-0.60
volume expansion coefficient at 20 °C, °C ⁻¹	182×10^{-6}
latent heat of fusion, J/g ^f	-11.80
hydrogen overvoltage, V	1.06
ionization potentials, eV	
1st electron	10.43
2nd electron	18.75
3rd electron	34.20
magnetic moment, ¹⁹⁹ Hg, J/T ^g	4.63×10^{-24}
magnetic volume susceptibility at 18 °C, cm ³ /g	1.885×10^{-6}
potential, V	
contact Hg/Sb	-0.26
contact Hg/Zn	$+0.17$
pressure, internal, MPa ^d	1.317
reflectivity, degree at 550 nm	71.2
refractive index at 20 °C	1.6–1.9
temperature coefficient of resistance at 20 °C, W/°C	0.9×10^{-3}
resistivity, at 20 °C, Ω·cm	95.8×10^{-6}
soly in water, µg/L	20–30
surface tension temp coefficient, mN/ (m·°C)(= dyn/(cm·C))	-0.19
viscosity at 20 °C, mPa·s(= cP)	1.55

^a Ref. 7.^b T_1 is the temperature of a gas molecule striking a surface which is at temperature T_2 , and T_3 is the temperature of a gas molecule leaving the surface.^c To convert kPa to mm Hg, multiply by 7.5.^d To convert MPa to atm, divide by 0.101.^e Relative to Pt–cold junction, 0 °C.^f To convert J to cal, divide by 4.184.^g Value is equivalent to 0.4993 µ_B.

Table 2. **Distribution of Stable Isotopes**^a

Isotope	CAS Registry number	Abundance, %	Isotope	CAS Registry number	Abundance, %
¹⁹⁶ Hg	[14917-67-0]	0.146	²⁰¹ Hg	[15185-19-0]	13.22
¹⁹⁸ Hg	[13891-21-0]	10.02	²⁰² Hg	[14191-86-7]	29.80
¹⁹⁹ Hg	[14191-87-8]	16.84	²⁰⁴ Hg	[15756-14-6]	6.85
²⁰⁰ Hg	[15756-10-2]	23.13			

^a Ref. 7.

Table 3. Thermodynamic Properties of Mercury^a

Property	Value
entropy, S_{298} , J/mol ^b	76.107
heat of fusion, J/mol ^b	2,297
heat of vaporization, ΔH_v , J/mol ^b	59,149
liquid mercury, 25–357 °C, J/mol ^{b,c}	
heat capacity, C_p	27.66
$H_T - H_{298}$	$-1971 + 6.61\ T$
$F_T - H_{298}$	$-1971 + 661\ T \ln T + 26.08\ T$
gaseous mercury, 357–2727 °C, J/mol ^{b,c}	
heat capacity, C_p	20.79
$H_T - H_{298}$	$13,055 + 4.969\ T$
$F_T - H_{298}$	$13,055 - 4.969\ T \ln T - 8.21\ T$
heat of vaporization at 25 °C, J/mol ^b	61.38
latent heat of vaporization, J/g ^b	271.96
specific heat, J/g ^b	
solid	
–75.6 °C	0.1335
–40 °C	0.1410
–263.3 °C	0.0231
liquid	
–36.7 °C	0.1418
210 °C	0.1335

^a Ref. 8.

^b To convert J to cal, divide by 4.184.

^c T in K.

Table 3. **Electrode Reduction Potentials of Mercury, V**

Equation	E^0 , volts
$\text{Hg}^{2+} + 2e^- \rightleftharpoons \text{Hg}$	0.851
$\text{Hg}_2^{2+} + 2e^- \rightleftharpoons 2\text{Hg}$	0.7961
$2\text{Hg}^{2+} + 2e^- \rightleftharpoons \text{Hg}_2^{2+}$	0.905

Table 5. **Diffusion of Metals in Mercury**^a

Metal	CAS Registry number	Diffusion rate, $\text{cm}^2/\text{s} \times 10^{-5}$	Metal	CAS Registry number	Diffusion rate, $\text{cm}^2/\text{s} \times 10^{-5}$
lithium	[7439-93-2]	0.9	silver	[7440-22-4]	1.1
sodium	[7440-23-5]	0.9	gold	[7440-57-5]	0.7
potassium	[7440-09-7]	0.7	zinc	[7440-66-6]	1.57
rubidium	[7440-17-7]	0.5	cadmium	[7440-43-9]	2.07
cesium	[7440-46-2]	0.6	thallium	[7440-28-0]	1.03
calcium	[7440-70-2]	0.6	tin	[7440-31-5]	1.68
strontium	[7440-24-6]	0.5	lead	[7439-92-1]	1.16
barium	[7440-39-3]	0.6	bismuth	[7440-69-9]	0.99
copper	[7440-50-8]	1.06			

^aRef. 7.

Table 6. **World Mercury Production by Country, 1978–1992, t^a**

Country	1978	1988	1989	1990	1991	1992
Algeria	1055	662	587	637	431	425
People's Republic of China	689	940	1200	1000	950	950
former Czechoslovakia	196	168	131	126	75	70
Mexico	76	345	651	735	720	700
Spain	1020	1716	1380	425	100	
Turkey	173	97	197	60	25	5
former USSR	2068	850	850	800	750	700 ^b
United States	833	379	414	562	58	64
former Yugoslavia		70	51	37	30	30 ^c
other	142	130	159	141	74	70
Total	6252	5357	5620	4523	3213	3014

^a Ref. 14.^b Sum of mercury production in Russia, Ukraine, and Kyrgyzstan (USSR dissolved Dec. 1991).^c Yugoslavia dissolved Apr. 1992. Amount shown in representative of Slovenia.

Table 7. U.S. Mercury Consumption, 1988–1992, t^{a,b}

Use	1988	1989	1990	1991	1992
batteries	448	250	106	18	16
chemical and allied products ^c	86	40	33	12	18
chlorine–caustic soda production	354	379	247	184	209
dental preparations	53	39	44	27	37
electrical applications ^d	207	172	103	54	124
general laboratory	26	18	32	16	18
industrial and control instruments	77	87	108	70	52
paints	197	192	22	6	^e
other	55	32	25	165	148
Total	1503	1212	720	554	621

^a Ref. 14.^b Use of mercury and mercury compounds for agricultural purposes was banned by the EPA in 1978, and use in paper and pulp is believed to have been discontinued.^c Includes uses such as catalysts, pharmaceuticals, and amalgamation.^d Includes electric lighting, wiring devices, and switches.^e By 1992, use of mercury and mercury compounds in paints was completely banned by the EPA.