GOLD AND GOLD COMPOUNDS

1. Introduction

The chemical symbol for gold (the Anglo Saxon and German term) is Au (for *aurum*, Latin for gold) with an atomic number of 79, it is listed as a group Ib metal in the periodic table, having one electron on its outer shell. There are six artificial isotopes having masses between 196 and 200, four of which provide significant radiation; radioactive ^{198}Au- is actively used for medical analysis.

The sparkling, sunny appearance of a solid found relatively pure on the surface of the earth and readily worked into attractive adornments has attracted humans to gold since the beginning of time. Gold adornments fashioned earlier than 3500 B.C. have been found on the Black Sea coast near Varna, Bulgaria. Its rarity made gold a status symbol in ancient times and a fiduciary asset in recent times.

The pecuniary relationship between gold and silver, the second most used monetary metal, has varied in terms of the apparent relative availability of these metals. Hammurabi, King of Babylon (ca 1915 B.C.), set the gold:silver ratio at 1:6. In Rome (ca 10 A.D.) it was 1:11. Sir Isaac Newton and Alexander Hamilton set it at 1:16. In 1930 it stood at about 1:60 (1). In 1999 it was ~1:56.

Sir Isaac Newton, Master of the Mint, Bank of England, declared in 1717 that an ounce of gold was worth 3 pounds, 17 shillings, and 10.5 pence. This rate stood, with only minor fluctuations, until 1930 (1).

The First Secretary of the U.S. Treasury, Alexander Hamilton, in his Report to the Treasury in 1792, proposed the adoption of a bimetallic (gold and silver) monetary system. The Coinage Act of 1792 made the dollar equal to 24.75 grains of gold or 371.25 grains of silver (a ratio of 1:15).

Alexander Hamilton proposed that the U.S. government assume the entire Revolutionary War indebtedness. Hamilton accomodated this enormous debt by denominating 40 paper dollars as one specie dollar. Thus by the stroke of a pen he reduced the national and state debts from about $400 million to $40 million in gold. By converting to gold he was able to refinance the debt at a comfortable 4% interest rate, which was within the ability of the fledgling government to pay.

In March 1848, California, which had just been purchased from Mexico for $15 million, was the site of a gold discovery, which by the end of 1849 amounted to over $10 million. It was the search for gold that accelerated the development of the western U.S. states and underwrote the immense expansion of world trade during the 1850s (2).

After the confederation of Canada in 1867, William H. Seward, Lincoln's Secretary of State, began negotiations with Czar Alexander II's minister to America for the acquisition of Russian America (Alaska). The price agreed was $7.2 million in gold.

Before 1834, because silver was overvalued by the U.S. Mint, the United States was on a silver standard. The Coinage Act of 1834 changed the weight of the dollar to 23.2 grains of fine gold, leaving unchanged the weight of the dollar in silver. Thus, from 1834 until the Civil War, suspension of specie payments, the United States was on a gold standard. Currency in gold was suspended during the Civil War for the creation of money to help finance the war (3).

In 1913, under peacetime conditions the Federal Reserve Act was passed allowing for the interconvertibility between paper money and gold. During World War I, the United States suspended interconvertibility. A worldwide gold standard was reestablished for a brief period in the 1920s, but the gold standard never again played the role that the framers of the Coinage Act had planned.

By 1929, most countries kept their monetary reserves in the form of balances of other currencies convertible into gold at fixed prices, notably sterling and dollars, rather than gold. The international effects of the depression became severe not only because the gold-exchange standard had rendered the international financial system more vulnerable to disturbances but also because it did not permit the inflow of gold to expand the U.S. money stock.

Severely affected were those countries that had the smallest gold reserves and whose financial structures were weakened by World War I. Britain abandoned the gold standard in 1931. In 1933, the United States suspended payments in gold and forbade the private holding of gold (legal price, $20.67/tr oz). A joint resolution introduced into Congress was passed June 5, 1933, abrogating the gold clause in public and private contracts.

On January 31, 1934, President Roosevelt, under the authority of the Gold Reserve Act, reduced the gold content of the dollar to 13.71 grains of gold. With the rate at \$35/tr oz, the gold stock in the U.S. Treasury rose from 200 million ounces in 1934 to 630 million ounces by the end of 1940.

The Bretton Woods Conference of 1944 proposed the elimination of protectionist trade policies, controls on capital movements, exchange controls, and competitive currency depreciations. Exchange rates were to be pegged within narrow margins to the dollar, and the United States would undertake to convert dollars to gold or the reverse at \$35/oz. Par values for currencies outside the United States were established. By 1958 the U.S. dollar had achieved the status of the reserve currency of the international economy.

However, by 1960, the U.S. gold reserves, pegged at \$35/oz, fell below the level of total U.S. liquid liabilities to all foreign holders of assets as denominated in dollars, and continued to fall. This coupling of shrinking U.S. gold reserves and an acceleration of the U.S. inflation rate undermined one of the basic underpinnings of the Bretton Woods agreement, the convertibility of U.S. dollars to gold.

On March 12, 1968, the U.S. gold reserve requirement was abolished. The United States continued to adhere to an official price of \$35/oz despite the rise in price in the open markets to \$42.60/oz.

A pattern of deficits and surpluses developed in 1970 and 1971 in which the U.S. capital account deficit grew dramatically. The dollar outflow accelerated, leading to the floating of European currencies.

A meeting at the Smithsonian Institution in Washington on December 17–18, 1971 led to revalued European currencies and a devaluation of the dollar to \$38/oz. Despite this, growth of money in circulation, inflation, and U.S. balance-of-trade payments soared, and on February 10, 1973, with foreign currencies floating that did not staunch the flow of dollars abroad, the dollar was again devalued to \$42.22/oz.

In June 1974, 10 European countries agreed that intercentral bank loans could use gold as collateral at the free market price \$159.10 (1974 average). The United States repealed the prohibition against gold holding by U.S. residents as of January 1, 1975. In August 1975, a committee of the International Monetary Fund (IMF) agreed that the official price of gold would be abolished, members would not be obliged to use gold in their transactions with the IMF, and that a part of the IMF gold holdings would be sold at auction (1975 average \$161.10) and another part be returned to the member countries in proportion to their quotas.

Gold is no longer the numeraire of the international monetary system. In July 1974, Special Drawing Rights were introduced in the IMF, which are valued in terms of a basket of national currencies, and were intended to replace both the dollar and gold (3).

On January 2, 1975, the New York Commodity Exchange (COMEX) began trading 100-troy ounce gold futures contracts. This effectively opened the free market for gold that functions today.

Since 1979, the U.S. Treasury has sold almost none of its gold reserves. In September 30, 1980 an audit of U.S. government–owned gold totaled 264,514,379.521 fine troy ounces. Since that time the only gold the Treasury has sold using U.S. reserves has been for commemorative coins. The one- and fractional-ounce Gold Eagle bullion coins sold by the Treasury are minted from newly mined gold from U.S. mines (Public Law 95-630, Nov. 10, 1979).

On the other hand, several countries, for example, Argentina, Australia, Belgium, Canada, the Netherlands, and the United Kingdom, have divested themselves of some or all of their gold holdings.

Although gold has lost its status as the world's numeraire, it will never lose its intrinsic value. Thus, in the developing world, low premium–high karat jewelry and the gold bar represent the major savings (if not total savings) of the average citizen—more than half of the world's population is in this category.

The future role of gold in the international monetary system as a reserve asset and as a determinant of the world's price level may depend on the performance of the domestic U.S. dollar (3) and/or the Euro dollar.

The rigorous performance demands of electronics, telecommunications, and aerospace systems created a new role for gold beyond that of a readily fungible asset. These demands have led to extensive research into the potential of its unique chemistry (44).

2. Occurrence

Gold is widely distributed throughout the earth in very small concentrations (5). In the crust it averages ~3 parts per billion (ppb), and in seawater it varies from 0.001 to 44 ppb (6). Mining for gold is economic only where there has been natural concentration by precipitation from hydrothermal solutions. These dissolve the metal and on percolating upward reach oxidizing agents that precipitate gold as a native metal in veins at or near the surface (7). Gold occurs primarily as a native metal, although often alloyed with other elements, usually silver. When the proportion of silver reaches ~20%, the alloy is termed *electrum*–this impure gold alloy was commonly use in ancient coinage. The most abundant natural minerals of gold are the tellurides ($AuTe_2$ and $AuAgTe_4$). Large telluride deposits are associated with volcanic intrusives, such as at Cripple Creek, Colorado (8,9).

Gold weathered out of rock naturally collects in stream beds as particles or tumbled into nuggets. This gold is readily separated mechanically in water by weight or by amalgamation with mercury. Known since ancient times as placer mining, it continues to this day (9).

Traditionally, gold deposits have been classified in terms of their host rocks (igneous, metamorphic, and sedimentary) or where they occur (veins, skarns, disseminations, or coproducts with other metals). Discoveries of highly disseminated gold deposits have now led to a new classification based on the oxidation/reduction state of the transporting fluid and its sources. As a consequence, gold geochemistry is the new prospector's tool (7).

Geochemistry accumulates local data on the temperature, pH, and concentrations of hydrogen sulfide and chlorine ions in fluids associated with hot-springs. These fluids solubilize the minute amounts of gold that are present in all rock types in the 0.1–0.2-ppb range. On reaching the surface in the presence of slightly alkaline rocks and a reducing environment (eg, high concentrations of carbon, iron, carbonates, and possibly arsenides), the gold ions precipitate out of solution as highly disseminated metal. Such deposits are being worked at McLaughlin, California, and at Alligator Ridge, Carlin, and Jarrett Canyon, Nevada, all highly disseminated hot-spring types (10,11).

As hotspring deposits appear in volcanically active areas where there is or was a hot spot, indications from surface-imaging satellites may be used to pinpoint them. These are confirmed by surface investigation (10).

Stratographic sections of typical gold deposits are described in the literature (12).

3. Sources and Supplies

Gold is found throughout the world. Alluvial gold has been worked in Siberian river beds since Neolithic times, contributing to Russia's impressive output over the centuries. Objects crudely fashioned from gold nuggets dating from about 7000 B.C. have been found in Mesopotamia. Gold artifacts of Egyptian origin date to 5000 B.C. It is estimated that the Egyptian mines between the Nile and the Red Sea yielded some 850 metric tons of gold over their millennia of operations (13).

The discovery of gold-bearing sands in Uzbekistan south of the Aral Sea led to the discovery of the Muruntau Mountain lode, a huge volcanic intrusion of quartz veins containing gold of exceptional purity. Both open-pit operations and underground shafts tap into this vast volcanic deposit, which produces some 80 tonnes of gold per year; it is the largest gold mine in the world.

In South Africa, extensive intrusions in igneous rocks and particles present in pre-Cambrian stream beds provide the country with the largest gold output in the world. The ancient placer gold beds lie tilted nearly 45° to the horizon, containing an average of ~7 g/t of "reef" material with some running as high as 15 g/t. In Anglogold's "western deep levels," pursuit of reef material has led to shafts >2 mi (>3.22 km) below the surface. Beginning with the Witwatersrand discovery in 1886 through 1996, South African mines have produced over 47,400 metric tons of gold (14).

3.1. World Resources. Of the estimated 130,000 metric tons of gold mined from historic times to the present, it is assumed that no more than 15% has been lost or is otherwise unrecoverable. Of the remaining 120,000 t, about 34,000 tons are held in central banks, and some 71,000 t are held in private hands as jewelry, bullion, coin, or are in industrial use.

The U.S. Geological Survey (USGS), estimates remaining gold resources worldwide to be on the order of 89,000 t, of this, South Africa may contain about one-half (15). The world reserves (recoverable with current technology) are estimated to be as listed in Table 1.

Table 1. **World Gold Reserves, t**

South Africa	18,500
United States	5,600
Australia	4,000
Russia	3,000
Uzbekistan	2,000
Canada	1,500
Brazil	800
Other countries	9,300
World total	*45,000*

4. Properties

Gold, atomic number 79, is a third row transition metal in Group 11 (IB) of the Periodic Table. It occurs naturally as a single stable isotope of mass 197, ^{197}Au, which is also formed via the decay of ^{197}Pt (half-life 20 min) formed in the irradiation of platinum with slow neutrons (16). The electronic configuration of gold is [Xe]$4f^{14}5d^{10}6s^1$. Common oxidation states are 0, 1, and 3. Selected properties are shown in Table 2 and 3 (17). Gold is characterized by high density, high electrical and thermal conductivities, and high ductility. One gram of gold can be drawn to 165 m of wire having a 0.02-mm diameter. Gold leaf 0.14 μm thick still exhibits the shiny color of gold. At least 26 unstable gold isotopes have been made; the most frequently used is ^{198}Au which has a half-life of 2.7 d.

Gold is the most noble of the noble metals. Other than in the atomic state (18), the metal does not react with oxygen, sulfur, or selenium at any temperature. It does, however, react with tellurium at elevated (ca 475°C) temperatures (19) to produce gold ditelluride [12006-61-0], $AuTe_2$, which is also found in the naturally occurring mineral, calaverite [37043-71-3], AuTe. Gold reacts with the halogens, particularly in the presence of moisture. At low ($\leq$200°C) temperatures, chlorine is adsorbed on the gold surface with formation of surface chlorides. The rate of further chlorination is limited by the rate of diffusion of Cl, or more likely, the diffusion of gold through this surface chloride layer. At higher temperatures, the reaction is kinetically controlled as gold chlorides sublime and fresh surface is continually exposed. At 700−1000°C, adsorbed Cl_2 dissociates into Cl atoms which then react with the surface (20). The chlorides are, however, unstable in this region.

Gold reacts with various oxidizing agents at ambient temperatures provided a good ligand is present to lower the redox potential below that of water. Thus, gold is not attacked by most acids under ordinary conditions and is stable in basic media. Gold does, however, dissolve readily in 3:1 hydrochloric—nitric acid (aqua regia) to form $HAuCl_4$ [16903-35-8] and in alkaline cyanide solutions in the presence of air or hydrogen peroxide to form $(Au(CN_2)^-$. These reactions are important to the extraction and refining of the metal. Similarly, gold anodes are solubilized in chloride or cyanide baths (see Metal anodes). Gold dissolves slowly in concentrated selenic acid at 68°C.

At high temperatures, attack by concentrated sulfuric and nitric acids is slow and is negligible for phosphoric acid. Gold is very resistant to fused alkalies and to most fused salts except peroxides. Gold readily amalgamates with mercury. Gold is very corrosion and tarnish resistant and imparts corrosion resistance to most of the commonly used gold alloys, especially to alloys containing 50 or more atom % of gold. Although gold is resistant to organic acids, some of the base metal containing alloys used in jewelry may become tarnished by perspiration and, in rare instances, cause allergic reactions (nickel itch).

Gold alloys also are subject to stress-corrosion cracking, especially alloys below 14 carat (58% gold). Jewelry items may have areas of high local stress that can induce cracking and corrosion in normally harmless environments such as solutions of hydrochloric or nitric acid. Stress-corrosion cracking occurs essentially as intergranular corrosion at unstable structural sites by an electrochemical mechanism (21) whereby the nongold components of the alloy become preferentially oxidized. Stress-corrosion cracking occurs primarily in

Table 2. **Gold Properties**

Property	Value
atomic weight	196.9665
melting point, K	1337.59
boiling point, K	3081
atomic radius, Au lattice, nm	0.1422
crystal structure	fcc
atoms/unit cell	4
lattice constant at ambient temperature, nm	0.407
interatomic distance at ambient temperature, nm	0.2878
density[a] at 273 K, g/cm^3	19.32
Brinell hardness (10/500/90), annealed at 1013 K, kgf/mm^2	25
modulus of elasticity at 293 K, annealed at 1173 K, MPa[b]	7.747×10^{4}
Poisson's ratio, as drawn	0.42
tensile strength, annealed at 573 K, MPa[b]	123.6–137.3
elongation, annealed at 573 K, %	39–45
compressibility at 300 K, Pa^{-1}[c]	6.01×10^{-12}
heat of fusion, J/mol[d]	1.268×10^{4}
heat of evaporation at 298 K, J/mol[d]	3.653×10^{5}
vapor pressure, Pa[c]at 1000 K	5.5×10^{-8}
at 1500 K	8.5×10^{-2}
at 2000 K	82
at 2500 K	4.9×10^{3}
at 3000 K	7.1×10^{5}
specific heat at 298 K, J/(g · K)[d]	1.288×10^{-1}
thermal conductivity at 273 K, W/(m · K)	311.4
thermal expansion at 273–373 K, K^{-1}	1.416×10^{-7}
electrical resistivity at 273 K, cm	2.05×10^{-6}
temperature coefficient of resistivity at 273–373 K, K^{-1}	4.06×10^{-3}
work function, J[d]thermionic	$7.69–7.85\times10^{-19}$
photoelectric	$8.17–8.76\times10^{-19}$
thermal emf,[e] mV, at Kat 373 K	0.92
at 773 K	6.40
1073 K	12.35
total emissivity at 493–893 K	0.018–0.035
susceptibility (magnetic) at 291 K, cm^3/g (=emu/g)	1.43×10^{-7}
Hall coefficient at 295 K, (· cm)/T[f]	-6.97×10^{-17}
entropy at 298 K, J/K[d]	47.33
standard reduction potential, V $\text{Au}^{+}+e^{-}\rightarrow\text{Au}$	1.69

[a] The commercially accepted value has been given. Measured values and density calculations from x-ray data show some variations.

[b] To convert MPa to psi, multiply by 145.

[c] To convert Pa to mm Hg, divide by 1333.3.

[d] To convert Pa to mm Hg, divide by 133.3.

[e] Emf values are given vs the reference-grade platinum of NIST (NBS Pt27) with the cold junction at the ice point.

[f] To convert T to gausss, divide by 1.0×10^{-4}.

Table 3. **Optical Properties of Gold**

	Thickness, μm			
Property	0.40	0.55	0.70	1.00
reflectance, %	38.7	81.6	96.7	98.1
refractive index		0.331	0.131	0.179
extinction coefficient		2.324	3.842	6.044

single-phase alloys. A remedy against it is stress relief by annealing; however, in the case of multiphase, low carat alloys, care must be exercised so that annealing does not lead to the formation of homogeneous solutions (see CORROSION AND CORROSION INHIBITORS; FRACTURE MECHANICS).

5. Extraction and Refining

Primary gold ores are usually classified as refractory (difficult to treat) or nonrefractory. Gold is extracted from nonrefractory ores, which contain free gold in a relatively inert matrix, by grinding or crushing and gravity concentration, then direct cyanidation (in agitated leaching in vats or spray leaching on open dumps or heaps) or by selective flotation (adsorption of gold-bearing ore particles to specific chemicals that float to the surface in an aqueous mix) (see METALLURGY, EXTRACTIVE, MINERAL RECOVERY AND PROCESSING), (22–24).

5.1. Conventional Extraction. The conventional recovery of the gold by the cyanidation process wherein finely ground ore is agitated in vats of 0.1% sodium cyanide solution. This process recovers over 85% of the gold. The pregnant solution is filtered and zinc powder added to precipitate the gold, which is filtered and deaerated by vacuum. An alternative method becoming more common is to conduct the pregnant solution through activated-carbon columns that adsorb the gold. The gold is stripped off the carbon by hot caustic soda. The stripped solution is shipped to a precious metals refinery for electrolytic purification (25,26).

Refractory ores contain interfering elements or minerals such as an activated type of carbon that tends to adsorb the gold cyanide complex, resulting in a loss in recovery of the metal. For such ores, direct cyanidation cannot be used. Recovery techniques are designed to meet the specific extraction requirements for the ore. For example, sulfide ores must be converted into oxidized form, typically by roasting under pressure oxidation, before the gold can be efficiently extracted by conventional methods (27).

Flotation is an important alternative to the use of cyanidation. Here, finely ground ore particles are treated with chemicals that selectively adsorb the precious-metal values and float them to the top of the vat. The floating matter is skimmed off, the chemicals removed, and the raw concentrate melted into a high precious-metal content bar for shipment to a precious-metal refinery (27,28).

5.2. Heap Leaching. The discovery of vast quantities of ore with highly disseminated gold particles, and the existence of large quantities of mine tailings from old less-efficient operations in the western United States whose values were too low for recovery by standard methods (under ca. 0.1 oz/ton of ore), led to the development in 1969 of heap/dump leaching by very dilute sodium cyanide solutions. The capital costs of heap leaching are a fraction of conventional milling, vat dissolution, and filtration methods (23,29,30).

Heap leaching is most efficient for relatively permeable ores roughly crushed into pieces of about 10–25 mm in diameter, dumped onto impervious pads with about 2 kg of lime per ton, and sprayed with 0.1% sodium cyanide solution. Attention must be given to the presence of clays and slimes (30–32). The precious-metal cyanides draining from the heap are collected and the solution treated with zinc to precipitate the gold, or flushed through activated-carbon columns which adsorb the precious-metal values, then stripped of the gold by hot alkali. Heap leaching recovers only about 70% of the contained precious metal; however, its use is cost-effective for very low grade ores (31,32).

By the 1990s heap/dump leaching had become the dominant process of precious-metal recovery from low grade ores throughout the world. Commercial operations in the United States, primarily in Nevada and California, operate heaps that cycle ore in the range 10–10,000 tonnes per week.

In all gold recovery processes, the valuable sodium cyanide is recovered and recycled.

5.3. Oxidation and Other Alternatives to Cyanidation.

Oxidation and the use of bacteria to oxidize ores is gaining favor over conventional roasting or pressure oxidation because, although slower, it provides improved gold recovery, is easily controlled by unskilled labor, is environmentally friendly, and has greatly reduced capital cost (23). Among the most considered alternatives to sodium cyanide is thiourea (12). Although it complexes faster than cyanide, it also complexes with other base metals, requires high concentrations, is rapidly oxidized on leach pads, is listed by the USEPA as a potential carcinogen, and may have a long-term stability in the environment (23).

5.4. Refining.

The gold-bearing material from the various ore concentration methods is smelted with fluxes that capture and remove impurities in molten slag to produce a gold-rich mixture of metals. Borax is added to the molten mixture and chlorine gas bubbled through it to convert the base metals into their chlorides, which are collected and removed in the slag. The gold remaining is about 99.5% pure.

To increase purity, the 995 gold is cast as an anode, placed in an electrolytic bath in which gold chloride/hydrochloride acts as the electrolyte and pure gold is deposited on a pure gold cathode. A purity of 9999 gold (99.99% pure) is achieved at this point. Repeating the process increases the purity of the gold. Substantial variations in the refining process are required to eliminate trace metals found in the ore (22,33,34).

5.5. World Gold Refining Capacity.

In 1991, there were some 107 gold refineries worldwide with a total capacity of over 4400 t. In 1996 with a world gold mine production of ~2300 t of raw gold, plus ca 640 t of old gold scrap, entering the refineries; thus considerable excess refining capacity exists. In western Europe during 1991 this excess capacity amounted to about 1680 t of raw gold, far in excess of the then European mine production of 65 t of gold, indicating significant competition for imported raw gold. In 1991, Latin America was the only area where mine production exceeded refinery capacity (35).

6. Manufacturing and Processing

It is mainly for electronics applications (such as for microcircuits and their connections) that gold is commercially supplied at extremely high purity (99.999%). For all other uses the pure metal received from the refinery is too soft, possessing unacceptable wear characteristics for brazes, decorative applications, electrical contacts, and jewelry. In order to provide the advantageous properties of gold to these applications, alloying with other metals is necessary.

6.1. Jewelry. Pure gold (24-carat or 100%), which is unsatisfactorily soft, is rarely used for jewelry. Gold is alloyed with other metals to increase workability and performance. Gold alloys sold in , exported from, or imported into the United States must be at least 41.6% gold (10-carat) to be permitted to carry the designation "gold." (see *U.S. Code of Federal Regulations*, Title 15, Section 295). Alloys below 42% gold exhibit poor tarnish and corrosion resistance.

Gold alloys required by the jewelry manufacturer must provide good casting and working characteristics, high strength, elimination of stress corrosion cracking, satisfactory long-term wear, and desirable color. Alloys over 80% gold (20- and 22-carat) possess unsatisfactory hardness and strength for normal jewelry. Alloys of 75% gold (18-carat) have superior tarnish resistance and the various additional metals provide advantageous working properties; these are the alloys of choice for the jewelry manufacturer (36,37).

The primary metals used for jewelry alloys are silver and copper. Gold forms a simple solid solution with silver, but with copper it forms intermetallic phases at high temperature, which, following quenching, yields a workable alloy. Subsequent heating of a AuAgCu alloy results in the formation of two solid solutions—AuAg and AuCu—which, depending on the composition following age-hardening, can achieve a Brinell hardness of >200.

A wide variety of metals have been used to create advantageous working properties. Cobalt inhibits grain growth (as does nickel, the use of which has been eliminated because of "nickel itch"), and small percentages of iridium, ruthenium, and rhenium are used as grain refiners in dental gold alloys. Zinc is commonly added as a deoxidizer, with boron and silicon similarly added to some casting alloys.

A unique jewelry alloy developed for the World Gold Council is the 99% Au, 1% Ti alloy (23.75-carat). When heated and quenched this alloy is very malleable and can be worked into the most intricate designs. Casting must be done under argon. On completion, the finished piece must be heated in argon to >500°C to age-harden the alloy into a high gold content durable metal (38).

The specific requirements of a jeweler-manufacturer should be discussed with the gold supplier. Details about suppliers and shipment practices can be obtained from The Manufacturing Jewelers & Silversmiths of America, Providence, RI 02903.

Guides for the Jewelry Industry, published by the Federal Trade Commission, Washington, DC 20580 (U.S. 16 CFR Part 23), discusses misrepresentation as to gold content, gold coatings, stamping (eg, 24 K), labeling, and so on.

In 1997 the worldwide use of gold for fabrication into carat gold jewelry and chains was over 3300 t (see Table 4) (39).

Table 4. **Consumption of Gold by Use in 1997, t**[a]

jewelry	3328
electronics	237
official coins	99
medals, etc	42
dentistry	70
industrial and decorative	114
Total	3890

[a] Ref. 39.

Electronics. Gold stands in a unique position in electronics. Its high conductivity and absence of corrosion are essential to the production and performance of electronic devices. Examples include: electroplated contacts and connectors, bonding wire and bumps [this is a new application of an old technique] for connecting computer chips, and solid gold targets for sputtering gold onto insulating substrates to form microchip circuitry and produce recordable compact disks.

Contact points and connectors are coated with gold to assure static-free transmission of digital data over switching points, friction contacts, and soldered connections. Electroplated gold technology requires aqueous solutions that produce uniform, fine-grained gold or gold alloy deposits with the required ductility and wear resistance. A wide variety of gold solutions are used for this technology (36,40). Electroless gold plating has also been developed for this application. A list of suppliers and shipment requirements may be had from The American Electroplaters Society, Orlando, Fl 32826.

Gold wire thinner than a human hair has been used to interconnect some 50 billion tiny microprocessor chips providing reliable performance to millions of personal and mainframe computers. It is a triumph of metallurgical research. The wire is 99.99% pure gold, but the remainder is critical to the performance of the wire. Beryllium, calcium, copper, silver, and other agents may be added to improve the wire's bonding performance in machines that can perform up to 120,000 connections per second.

The addition of these metals improves the shape of the molten ball, which welds the wire to the chip, reduces breakage during pulling of the wire from the welded joint, and improves the strength of the cold-crush welds at the other end of the wire that are swaged onto the leadframe (41,42).

Metallurgical uniformity of the wire as it leaves the production line is essential (43). In 1997 alone, these connecting wires required ca 67 t of gold (ca 2×10^6 troy ounces), worth over \$600 million. However, each personal computer requires only a few cents, worth of gold to assure reliable, long-term performance. The number of gold interconnections has been increasing about 12% per year.

Sputtering target gold disks are supplied in at least 999.99 fine. Placed in an evacuated chamber with only an inactive gas such as argon present, a static electric charge drives the gas atoms to hit the target, striking off gold atoms, which then hit the object being coated with such force that they permanently adhere to it. The sputtering process provides greater adherence and a finer grain size than do other coating techniques. This process has largely displaced wet electrodeposition in the semiconductor industry. Instrumental chemical analyses measuring impurities in parts per billion are used for quality control of these targets (44).

Sputtered gold coatings provide microcircuit wafers with highly conductive circuit paths, permanent corrosion barriers, and high thermal reflectivity. Such coatings are found on visors for firefighters and astronauts and on transparent fighter plane canopies to protect pilots against intense solar radiation. Sputtering also provides the smooth gold surfaces required for recordable compact disks. Information on manufacturers may be obtained from The Gold Institute, Washington, DC 20036.

The worldwide use of gold for electronics in 1997 exceeded 237 t (39).

Brazed Components. The ability of gold to wet and therefore form strong bonds with many other metals makes gold an especially advantageous braze metal for applications from jet engine components to jewelry. The standard jet engine braze is 82% gold and 18% nickel, a most ductile and tough alloy that does not crack under extreme heat, shock, and vibration. Gold brazes have such important properties as (*1*) the ability to wet Cu, Ni, Fe, Co, Mo, Ta, Nb, W, and their alloys; (*2*) production of strong, ductile joints able to withstand extremely high operating temperatures without excessive interalloying; (*3*) freedom from forming refractory oxides; (*4*) exceptional resistance to corrosion; and (*5*) high malleability for forming into convenient shapes, such as rings, foil, and wire for high-speed brazing (36).

Ongoing research is conducted by braze suppliers who are active with the American Welding Society, Miami, FL 33126. U.S. consumption approaches four tons.

Dentistry. Gold is one of the few metals that will not react with body fluids and this combined with its malleability has made its use for tooth restorations ideal since ancient times. Information about these alloys may be had from the American Dental Association, Chicago, IL 60611.

In 1997, worldwide use of gold for dentistry amounted to >70 t, with Japan consuming the most, followed by Germany and the United States.

Ceramic Decoration. Fired-on bright gold decoration for ceramics began in the 1830s. Today's technology permits mass production and even use by amateurs to achieve perfect results. Liquid gold preparations burn off cleanly, providing mirrorlike bright gold films about 0.1 μm thick. A considerably heavier and more durable layer of gold, known as burnished gold, may be applied using gold-rich frit preparation. These films are 3–6 times as thick as bright gold (0.3–0.6 μm) and provide the greater durability and abrasion resistance required of restaurant china. Both types may be printed on decalcomanias to provide mass produced designs. A three-dimensional appearance can be achieved by the application of frit (45). A suppliers list may be had from the Society of Glass & Ceramic Decorators, Washington, DC 20006.

In the United States this consumption amounts to about six tons per year.

Gold Leaf Decoration. The earliest (at least 3000 B.C.) of the manufactured gold products is supplied as hand or mechanically beaten gold of at least $23\frac{1}{2}$ carats in sheets that are about 3 millionths of an inch thick, requiring about 250,000 sheets for an inch in thickness (46). Gold leaf is applied over a slow-drying varnish; at the moment it is tacky, the gold will stick to it and the gloss of the varnish is retained in the leaf.

Table 5. **World Gold Mine Production in 1997, t**

Africa	630
North America	520
Central and South America	312
Oceania	326
Asia	216
Europe	33
Western world	427
World total	*2,464*

Table 6. **The Top Ten Gold-Producing Countries in 1997, t**

South Africa	489
United States	351
Australia	311
Canada	168
China	157
Russia	137
Indonesia	101
Uzbekistan	82
Peru	75
Brazil	59

A suppliers list may be obtained from the Society of Gilders, Norcross, GA. 30071.

7. Production

The yearly world mine production survey conducted by The Gold Institute provides gold-production data from 72 countries with projections for the ensuing four years (47). The most productive areas are listed in Tables 5 and 6.

Gold production is expected to gradually decline in South Africa but increase in Latin America and Asia. The Gold Institute's *World Gold Mine Production 1997–2001* survey (47) shows significant projected increases in gold production from Peru, Brazil, Chile, Indonesia, Papua New Guinea, and the Philippines.

8. Economic Aspects

Gold as a store of value is related to its rarity. It is estimated that all the gold mined since the earliest times is about 130,000 metric tons (1) The world gold mine production for 1998 was estimated be over 2529 t, with the world total fabrication demand for all gold products at about 3770 t (39). The shortfall is made up by recycling scrap (see RECYCLING). All manufacturing sectors, except official coin production, show increasing consumption of gold.

The Bretton Woods Agreement (1944) established a gold-exchange system based on the parity of $35 U.S. per one troy ounce of gold. The agreement created the International Monetary Fund (FMF), which consisted of a financial reserve supplied by several countries. The reserve was made up of 25% gold and 75% national currencies (48).

In 1971, the United States, the last country to do so, suspended the convertability of its currency into gold. A free market became effective in 1973 with gold sold at $89/tr oz. Gold ownership by U.S. Citizens was restored by Congress in June 1974 and signed into law on December 31.

The International Jamaica Agreement of 1976 ended the parity of currencies with gold, which allowed the price of gold to float on the exchange markets. The Special Drawing Right replaced gold as a parity standard and gold was demonetized as a world currency. The IMF was then placed under obligation to sell one-third of its gold assets ($30 billion in gold was retained as part of its reserves).

8.1. The Gold Mining Industry. With the price of gold fluctuating in terms of market price rather than cost of recovery, the mining industry finds its operating profits fluctuating similarly. When ores play out, the search to open new mines in new areas entails regulatory and political difficulties, delays in awarding of permits, taxes, and questions about local mining law reform, all of which impact a mining company's financial risk and potential profitability (12).

The scale of the capital investment involved in opening new gold mines is illustrated by the cost of developing 10 new mines in the United States that started production during 1989–1993. The total cost of opening the 8 new surface or open-pit mines was $369.7 million, and the cost of opening the two underground mines was $87.4 million. The gold industry invested $17 billion in the United States for property development during 1980 and 1998 (49).

8.2. Risk. To overcome the risk that the price of gold may drop below mining costs by the time the gold is mined and refined, mining companies use a market technique known as "hedging." Here a company arranges with a buyer to purchase its future production at a price that will cover its anticipated expenses. The buyer may lose money if the price falls, or the company may lose money if the price rises but the company has covered its potential risk exposure (49, 50). In 1997, producers hedged some 581 t of gold production (39).

The economic accessibility of gold from an ore body is directly related to extraction costs that vary from one type of ore to another. A 1987 study of the processing of gold from its ores showed fairly uniform costs for the various techniques used (51) (see Table 7).

Production costs vary not only from mine to mine depending on the ore, mining difficulties, processing techniques, labor, administration, royalties, property and mining taxes but also by concurrent investment in continuing exploration to develop the property. These are termed "cash" costs. To these must be

Table 7. **Cost Comparison of Gold Ore Processing**

Mine type and extraction	Median production costs $/oz
underground, flotation	216
underground, cyanidation	223
open-pit, flotation	217
open-pit, cyanidation	200
open-pit, heap leach	228

added "noncash" costs, which include depreciation, eventual reclamation, and mine closing expenses, in order to calculate a "total" cost.

For the year 1997, cash costs for U.S. gold mines averaged \$250 per troy ounce and the addition of non-cash costs brought the total costs to \$315/oz (39). The average London PM fix for 1997 was \$331.29/poz.

The world average cash production cost for an ounce of gold in 1997 was \$250 for operating mines, a 14% decrease over 1996 (which was \$286). The average total cost in 1997 was \$315, a 4% decrease over 1995 (which was \$327). These decreases were the result of stringent cost-cutting measures to maintain profitability. The average London PM fix in 1997 (\$331.29) had dropped 17% from 1996 (\$387.87) (39).

9. Grades, Specifications, and Quality Control

To guard against fradulent gold bars entering international trading markets, the London Bullion Market Association (LBMA) in concert with international bullion market associations worldwide has established requirements for "good delivery bars," which is defined by the LBMA as being the product of a refiner/assayer approved by the LBMA bearing the assayer's stamp (ingot mark) and its serial number, Good delivery bars are at least 995 fine (99.5% pure gold), between 350 and 430 troy ounces, with the precise weight and fineness stamped on each bar, and stamped with the ingot mark and bar number of an "approved refiner" which must have (*1*) been in the refining business for at least years, (*2*) an annual production of gold not less than 10 metric tons in the form of 400-oz gold bars, (*3*) an international reputation as a gold supplier producing at least 10 metric tons per year, and (*4*) have a net worth of at least 10,000,000 pounds Sterling (52).

Gold bars that have not been refined and assayed by an LBMA approved refiner/assayer are not traded on the London (LBMA), New York (COMEX), Tokyo (TOCOM), and Zurich (ZGM) international trading markets. Similar standards are also applied by the Sao Paulo, Hong Kong, Thailand, and Japan trading associations. Privately traded bars are not subject to these standards.

The purchase of gold in the world's metal markets, such as the London Bullion Market Association or the COMEX Division of The New York Mercantile Exchange, is set as a contract between the purchaser and the precious-metal refiner whose hallmark is stamped on the bar. COMEX and all the precious metal market organizations look to the integrity of the refiner, not just the physical product itself, in offering gold to open-market trade. Contracts through commodity exchanges are fulfilled by shipment from the refiner or an approved warehouse to the purchaser using an approved carrier.

Gold not refined by an approved refiner/assayer and offered for sale between private parties may be assayed privately. COMEX, approved assayers are: Ledoux & Company, Teaneck, New Jersey; Alex Stewart Inc., Clark, New Jersey; and A.H. Knight, St Helens, England, and Spartanburg, North Carolina.

Specifications for gold bullion, brazing alloys, electric contact alloys, and other parameters are published by American Society for Testing and Materials (ASTM), the American Welding Society, Japanese Industrial Standards, Society of Automotive Engineers (SAE) (Aerospace Materials Specifications), and U.S.

Dept. Defense (DOD). Voluntary specifications for gold bullion and gold alloys include ASTM B562, grade 99.5 refined gold, grades 99.95, 99.99, and grade 99.995 have specific impurity limits assigned to each grade (53).
SAE/UNS P00100, gold alloy, Au min 99.0, Ti 0.8–1.0, a very malleable alloy with hardness and durability for jewelry applications. The SAE/UNS system lists the compositions of 36 standard jewelry alloys (54).

The most reliable quantitative method for determining the purity of gold is the fire assay (55,56). However, as this is an expensive and time-consuming technique, instrumental methods for routine quality control are often used. For these, the fire assay serves as the referee method.

The high-purity assay required for COMEX certification is usually done using emission spectroscopy (57).

Where extremely high purity (99.999% or better) gold is demanded, for example for electronic applications, emission spectroscopy (56–59), inductively coupled plasma (60), and glow discharge mass spectroscopy (61) are used for evaluation. The inductively coupled plasma method is noted for its fast results, simplicity of operation and does not require the interpretation of a photographic plate.

For routine evaluation and rapid detection of fradulent gold bars and coins, frequency of resonance, which is dependent on specific gravity, modulus of elasticity, and volume, is measured by a device developed by Degussa, the Digor system (62). An electromagnetic detection device developed by Barringer Research is used by banks and metal markets, measures an electromagnetic response from the bar. Using a known pure gold bar of the same volume as a reference standard, rapid detection of inclusions and even bubbles is revealed (63).

9.1. Dentistry. Most casting alloys meet the composition and properties criteria of specification no. 5 of the American Dental Association (64) which prescribes four types of alloy systems constituted of gold–silver–copper with addition of platinum, palladium, and zinc. Composition ranges are specified, as are mechanical properties and minimum fusion temperatures. Wrought alloys for plates also may include the same constituents. Similarly, specification no. 7 prescribes nickel and two types of alloys for dental wires with the same alloy constituents (see DENTAL MATERIALS).

10. Analytical Methods

A total quantitative determination of the gold values in a sample can only be made using the “fire assay”. The fire assay has been the standard reference method to determine the proportion of gold in a sample since ancient Egyptian times. Other methods are capable of determining only surface components of a sample, such as surface composition, but not its totality.

All ores, concentrates, alloys, and scrap samples can be analyzed by the “fire assay.” Accurate determinations can be made of gold concentration from 5 ppm to about 100%. With today’s refinements, a skilled analyst can achieve an accuracy in the amount of 0.05 part per 1000 within the same sample, an accuracy of 0.10 part per 1000 between samples, and 0.2 part per 1000 between laboratories.

In the fire assay a fluxing material is added to the sample that has been wrapped in silver-free lead and heated to >1,000°C to oxidize and dissolve all base metals. A specified addition of silver, a powerful oxidizer, is added before cupellation to convert all base metals present into their oxides, which are absorbed in the bone ash cup (cupel), leaving behind only the noble-metal values for wet chemical analysis (4,55,56,65–68).

When the gold sample contains other noble metals such as Pt or Pd, a reducing agent is used to remove the gold, then the Pt or Pd is dissolved for quantitative evaluation. Pt and Pd are checked by instrumentation to determine whether gold is being carried with them. If so another separation is made to determine how much gold is being carried through. Then the Pt or Pd is checked again to be sure that no gold is present.

10.1. Quality Control. For bullion and jewelry, the fire assay is sufficient for quality control of 999 fine. For 9999 or 99999 fine, requirements set by the electronics industry, tests for impurities are made by inductively coupled plasma (69–71). When impurities in the parts per billion range must be identified, for such applications as gold sputtering targets for electronics circuitry, glow discharge mass spectroscopy is used (61,1).

The inductively coupled plasma technique functions on the same principle as emission spectroscopy (73–75), but uses solutions that are vaporized in a 8000–10,000-K plasma in argon. This technique is capable of analyzing many elements simultaneously, such as for determining low levels of other metals in scrap. It is fast, is simple, and does not require an interpretation of photographic plates. The combination with the mass spectroscope provides a powerful analytic tool.

Mass spectroscopy identifies elements by their reaction to a magnetic field. When used in combination with emission spectroscopic techniques, a quantitative assay of trace elements can be made. If identification of trace elements in the ppb range is required, the glow discharge mass spectroscope is used.

10.2. Fingerprinting Gold. The Anglo American Research Laboratories, Ltd., Crown Mines, South Africa, was established in 1993 to develop a reliable means to determine the provenance of gold. Using a laser beam, surface atoms are vaporized from a sample and transported by a stream of argon into a radiofrequency coil that raises the temperature of the atoms to 7000 K. The resulting ions are focused into a high vacuum quadrupole mass spectrometer where they are separated on the basis of their differing mass:charge ratios. On emerging from the mass spectrometer the ions strike an ion detector and a spectrum of signal intensity versus atomic mass is generated (76).

The procedure was developed to identify the source of pilfered gold as each mine has a distinctive proportion of trace elements. It has also found use to identify the geological source of ancient gold, the sources of other precious metals and of nonmetals, such as ivory, rhinoceros horn, and crude oil.

11. Recycling and Disposal

Gold is the most eminently recyclable material because of its high value. As it does not corrode nor dissolve under normal conditions, reprocessing is no more

Table 8. **Supply of Gold from Old Gold Scrap, in 1997, t**

Europe	62
North America	59
Latin America	20
Middle East	163
Indian subcontinent	79
Far East	182
Africa	8
CIS/Soviet Union	16
China	18
other countries	4
Total	*611*

difficult than winning gold from its ores. There is a steady return of gold into the market from worn out jewelry and obsolete industrial products. For example, in the Middle East and other parts of Asia, it is common practice for individuals to exchange old gold ornaments for new at little more than the cost of manufacture. In some countries gold ornaments and small pieces of gold are considered an individual's asset store, and upgrading their visual appeal is fashionable. Recycled jewelry represents by far the largest proportion of scrap gold (39).

Gold is critical to the long-term performance of electronic components. When the electronic components become obsolete, their gold values can nevertheless be substantial and therefore these components are returned to refiners for recovery of gold values using the same refining processes as those for gold ores; specifically, they are ground into fines, and treated to extract the gold from the less valuable material.

Other sources of gold for recycling are spent plating solutions, industrial scrap, recycled jewelry, and wastewater (77) (see CYANIDES). The supply of scrap gold from all sources processed in 1997 is shown in Table 8 (39).

12. Environmental Concerns

Pure gold is totally benign to the natural environment. Winning of gold from its ores when chemicals are used poses problems related to the chemistry of extraction.

12.1. Extraction by Sodium Cyanide. The clear superiority of sodium cyanide over all other methods to extract gold from its ores in terms of safety, environmental exposure, and ease of handling led to its worldwide use by 1890 (24). In the commercial extraction of gold from its ores, all operations involving cyanide are held within the confines of plant operations. With the advent of heap leach operations, cyanide solutions are more exposed to the environment and tightening its control is important (26,76,78).

In heap-leach operations where ore is heaped on impervious pads, cyanide can evaporate and spillage is possible; therefore, concern is directed toward environmental impact. Studies have verified that a number of naturally occurring physical and chemical mechanisms can result in significant attenuation and degradation of cyanide in solutions passing through soils. Studies have shown that clay liners for heap-leach pads have a natural cyanide degradation capacity that may be enhanced by the addition of carbonaceous and other materials (103) (see CYANIDES).

Most mines treat cyanide-treated tailings with ferrous sulfate to form the insoluble Prussian Blue. Also widely used is the patented Inco SO_2/air process system, which removes the cyanide through oxidation. Ozonation results in no undesirable byproducts; however, iron cyanides are not readily oxidized. Bacterial degradation of both complex cyanides and thiocyanite is successfully under way at a the Homestake Mine's cyanide wastestream in Lead, South Dakota, but the process is slow. Many other methods are possible, but costs, limitations of efficacy, and undesirable reaction products are limiting factors (24).

13. Health and Safety Factors

13.1. Therapeutic Gold Complexes.

The unique therapeutic effects of gold compounds can be related to their chemical properties. As one of the group IB transition metals, gold forms a large number of coordination complexes, and all the therapeutically active gold compounds in current use coordinate monovalent gold with primarily sulfur- and phosphorous-containing ligands. In the ligand exchange reactions, the compounds of gold react to block or redirect the biochemical reactions associated with certain diseases. The gold complexes employed to treat rheumatoid arthritis inhibit those detrimental reactions attributable to the action of lysosomal enzymes that contribute to these connective-tissue disorders.

Of the remittive and antiinflammatory agents available for the treatment of arthritis, gold salts have provided a most effective means in the manangement of this severe progressive disease. The unique chemical affinity of gold for endogenous sulfur ligands appears to inhibit, alter, or otherwise affect important reactive sites that mediate inflammatory and immunologic events operative in rheumatoid arthritis. Data from nuclear magnetic resonance spectroscopy suggest that gold salts have the ability to transport, store, and release reducing equivalents (thiols and phosphines), enabling increased coordination, which affects and influences the immune function (79).

Gold–sulfur complexes have also been found to be beneficial in the treatment of psoriatic arthritis, discoid lupus, pemphigus vulgaris, and bronchial asthma. In view of the diverse endogenous reactions of the aurous complexes, further investigation should prove rewarding for wider applications in medicine (79).

Research into the reaction of gold compounds with enzymes such as myleoperoxidase indicates that the gold is being oxidized from Au^{1+} to Au^{3+}, which has a specific reaction with the immune system. Studies are being conducted to determine what contribution this higher oxidation state of gold makes to the mechanisms of immunotoxic and therapeutic action around the inflamed sites and to the inhibiting of the lysosomal enzymes that contribute to connective tissue disorders (80,81).

Gold dicyanide, in combination with other drugs, retards HIV production in vitro (82). It is being evaluated as it is rapidly taken up by the cytosol of red blood cells and other biologically relevant material. Gold dicyanide can be found in the blood of all patients being treated with such gold drugs as auranofin, Solganol, or Myochrysine, indicating that it could be a significant product of gold metabolism.

Diphenylphosphine ethane gold was developed to provide an antitumor activity analogous to that of cisplatin. The compound in *in vitro* testing displayed some antitumor activity (83,84).

Metallic gold has for centuries been used for tooth restorations. Its alloys provide a benign, malleable metal well suited for this application (76,85).

Gold is ideal for coating surgical implants where biological inactivity relative to body fluids is imperative. Examples are heart pacemakers and plugs for newly pierced-ears.

The advent of nanogold technology (ca 1–3 millionths of a meter in diameter) has spawned new applications for gold. Nanosized particles of gold on which biologically active material are adsorbed are accelerated to supersonic speed by a helium gas jet in a hand held device. The gold and its adsorbed material is propelled through the human skin or plant walls directly into the target tissue layers. Gold has the required adsorptiveness to firmly hold small pieces of DNA, it is biologically inert, never associated with any toxicity so it is very safe, and it has sufficient density to carry DNA transdermally into the target cell without harming it. Once inside, the cell's natural functions work with the DNA and the gold is abandoned. Patents for the device are held by PowderJect Vaccines, Inc., Madison, Wisconsin (85).

Karat gold jewelry alloyed with other metals to increase its hardness and provide a range of colors is benign. However, white gold alloyed with nickel may result in a temporary dermatitis or "nickel itch." According to a national study, 2.5–5% of the general population is sensitive to nickel (86). To avoid this effect, nickel-free white gold alloys have been developed, substituting silver, palladium, zinc, and/or germanium (87).

Denmark, Germany, and Sweden have banned the sale of any item that will release nickel onto the skin at a rate exceeding 0.5 $\mu g/cm^2$ per week. The European Economic Community has issued a directive prohibiting the presence of more than 0.05% nickel in jewelry that may come in contact with an opening in the skin (87).

14. Uses

The fact that gold possesses a unique combination of advantageous properties [resistance to corrosion (best of all metals), electrical conductivity (third highest of all metals), infrared reflectivity (best of all metals or materials), thermal conductivity (third best of all metals), plus high malleability and ease of plating by several means], explains its wide application (40,88,89) despite its cost. The worldwide consumption of gold is given in Table 9.

14.1. Jewelry. Its oxidation-free, highly reflective, metallic sunlike luster makes gold the most desirable metal for jewelry and longlasting personal decoration. Over 3328 t of gold were used for this purpose worldwide in 1997 (4,36).

Table 9. **World Gold Fabrication in 1997, t**[a]

North America (USA and Canada)	850
Latin America	313
Europe	846
East Asia (Japan, etc)	781
Middle East	734
India and nearby countries	747
Africa	47
Australia	17
China	249
Soviet Union & CIS	298
World total	*3890*

[a] Ref. 39.

14.2. Electronics.

The thrust of electronic device construction is toward subminiaturization. Despite the continuing reductions in size of these high density components, superior performance requires complete freedom from corrosion that might occur when parts are exposed to the air prior to assembly and soldering. The use of gold coatings for corrosion-free surfaces for soldering, and static-free contacts and connections has been standard since the beginning of electronics. Now the use of submicron-sized particles of gold is being applied to the fabrication of subminiature electronic components which, despite their decreasing size, demand equally flawless transmission of digitized data (40,90).

Contacts and connectors form the largest proportion of the 237 t of gold used worldwide in electronics during 1997 (39,91). The U.S. Bureau of Census reports that the U.S. market for metal contacts, precious and other (product code 36434), reached $259.4 million in 1995.

Consumption of 99.99% pure gold wire used to connect microprocessing chips with their lead frames (which are attached to the motherboards of personal computers, etc) has grown with the expansion of electronics manufacture (40–42). The installation of 25-μm-diameter wire requires instantaneous welding onto the microchip on one end and swaging to the lead frame on the other by robotic machines at speeds up to 120,000 connections per second. Its manufacture has become a technological specialty. Worldwide, about 4×10^{12} wires are bonded per year, consuming some 50 t of gold annually (39). The use of gold bumps as connectors may become substitutes for this application.

Gold contacts and connectors are standard in new automobiles for engine control (about 200 gold-coated contacts for the efficient control of fuel, temperature, oil pressure, etc), wheel traction controls (about 160 contacts to balance power to wheels, and prevent spinning and hence loss of traction), and ride control (balance of car). Gold-plated contacts and connectors activate airbags in over 6×10^6 cars, assuring positive electronic response over the minimum 10-year or 150,000-mi (241, 395-km) minimum life-design standard for these safety systems.

The transmission of digitized data, ranging from international financial transactions to email (electronic mail) video images, has made the use of gold contacts and connections within electronic switching modules in telephone central stations essential. Likewise the billions of domestic and commercial miniature telephone jacks produced annually are gold-plated for long-term digitally-pure transmission over the connection. Those interested in high fidelity sound systems use gold-coated connectors to eliminate the generation of static noise between components.

Gold's superior electrical conductivity, lubricity, and freedom from oxidation are exploited for sliding contacts in the dual-spin satellites where one portion of the satellite must spin for stability and the other must direct its solar panels to the sun (40).

14.3. Brazing. Gold alloys provide brazing filler metals wetting a wide range of metals and ceramics at temperatures considerably below the melting point of the metals and thermal degradation of the ceramics being brazed. The joints formed are advantageously tough, shock-resistant, and ductile (no cracks to repair), with high electrical and heat conductivity. The earliest and widest used jet engine braze is 82% gold and 18% nickel. Commercial gold braze alloys incorporate Pd, Ni, Co, Cu, Mn, and Ti. One 35% gold alloy braze carries liquid hydrogen through 4 mi (6.44 km) of fine tubing to cool the inside walls of the space shuttle's engine nozzle. In that reaction chamber temperatures reach a steady 3300°C (6666°F), far above the melting point of the shuttle's structural metals (1400°C, 2500°F).

A 1990 survey indicated a U.S. consumption of about 47 t of gold for brazing alloys.

14.4. Decoration. The use of gold leaf to protect artistic and architectural masterpieces has been practiced since ancient times. Properly applied gold leaf on domes, commercial buildings, and statues will last for over 25 years outdoors before touchup is required; interior decoration will last indefinitely (36,40).

14.5. Corrosion Control. Gold's inactivity has made it a prime candidate for linings of reactor vessels in which severely caustic chemical reactions take place.

14.6. Hydrogen Barrier. The inactivity of gold combined with its large atomic size blocks the flow of hydrogen atoms through it. In the space shuttle, a layer of gold on the hydrogen fuel pump impellers, which handle 113 tons of hydrogen fuel, blocks those tiny atoms from reaching the impeller alloys. Should hydrogen contact the impeller alloys, embrittlement would occur and within a few seconds the impellers would shatter, leading to failure of the mission.

14.7. Solar Heat Control and Space Satellites. In the space vehicle gold is used (*1*) in the conductors in the computer microcircuits, (*2*) for connectors and contacts for circuit boards and components, (*3*) for thermal control to reflect away the heat from the sun that would otherwise overheat and degrade the function of a satellite's instruments and position control devices, (*4*) to conduct away (by electrically grounding) external radiowave or solar electrical bursts from interfering with the satellite's electronics, and (*5*) to provide sliding surfaces, because gold, which does not oxidize, will not cold-weld to oxidized metals (40).

In the instruments within the space vehicle, gold is used on the surface of the infrared and visible light detector elements to collect the input energy. These charge-coupled devices (CCDs), which are also the heart of the videocameras (camcorders) sold in electronics shops, are the cameras of the satellites.

14.8. Medical Uses. Gold has found wide use in dentistry for tooth restorations both as foil and powder. Its use worldwide amounted to over 70 t in 1997.

In medical and biological research, gold particles have revolutionized their procedures. Particles with an average diameter of 1.6 μm will adsorb proteins or other organics allowing researchers to track exactly where drugs react with body tissues to determine how best to provide healthful service.

These nanometer-sized gold particles (about 1–3 millionths of a meter in diameter) also adsorb biologically active materials such as those used to provide vaccinations. Here the nanosized particles of gold in a handheld device are accelerated to supersonic speed by a helium gas jet. The gold and its adsorbed material is propelled through the skin directly into the target tissue layers. Gold has the required adsorptiveness to hold small segments of DNA. As it is biologically inert, it is very safe with sufficient density to carry DNA transdermally into the target cell without harming the cell. Once inside, the cell's natural functions work with the DNA and the gold is abandoned (94). Patents for the needleless injection device are held by PowderJect Vaccines, Inc., Madison, Wisconsin.

Gold particles are also being used to carry DNA molecules for insertion into plants to stimulate growth, increase productivity, and provide them with greater disease resistance. And gold particles coupled to single strands of DNA can be used for pathogen identification, or point-of-site DNA diagnostics. They have the potential to help synthesize materials on an atom-by-atom scale. Colloidal gold containing radioactive Au-198 is actively used for medical analysis.

Arthritis sufferers have been relieved by gold drugs such as Myochrysine (gold sodium thiomalate) and Solganol (aurothioglucose), which bring the immune system back to normal function, reversing the cartilage and bone destruction caused by rheumatoid arthritis. These drugs are coordination complexes of gold (not gold salts where the gold is a free ion). The most recent antiarthritic gold complex is auranofin, developed by Smith Kline & French; the first gold compound to be taken orally for the treatment of arthritis, replacing gold drug injections (95,96).

Dicyanogold [$Au(CN)_2$], which is a normal byproduct of human metabolism, is a potential anti-HIV treatment because it retards the reproduction of HIV (97).

Noninvasive thermometers to measure body temperature rely on thermal energy radiated from the eardrum through a small gold-lined pipe inserted into the ear cavity. The heat is reflected by the gold without loss into the temperature measuring device.

14.9. Infrared Reflective Surfaces. Gold is the most infrared (heat) reflective metal. It is extensively used, for example, in the interior cavities of lasers to focus all the heat energy into the lasing crystal and increase its efficiency. Gold is widely applied in the space satellites to reject solar heat from components, electronics, and instruments. It is also used on commercial aircraft windshields and fighter plane canopies not only to protect the pilots from intense solar radiation, but to provide a conductive surface to heat the transparent surfaces and clear them of frost. It has been used for architectural glazing to reflect away the heat of the sun and reduce summer heat intake and winter heat loss (40).

Gold-coated reflectors are used in automobile paint-drying ovens to flashoff water from water-based paints. The gold coatings reflect nearly 99% of the thermal energy generated by heatlamps to cure automobile paint, markedly reducing heat loss through the oven walls.

The new twin Keck telescopes built on top of Mauna Kea in Hawaii each use a 21-in (53.34-cm) gold-coated secondary mirror to maximize the reflection of the faint infrared radiation from outer space. The gold-coated mirror will resolve infrared images with 2–3 times greater precision than any other telescope.

14.10. Lubricative Surfaces.

Dual rotating satellites require electrical contacts between the portion spinning for gyroscopic control and the antenna section pointed toward earth. The rotating electrical contacts use gold because it will not cold-weld in space with dissimilar metals that have thin oxide layers. The gears in space satellites used to point experiments in specific directions and the slip rings of large control mode gyroscopes have surfaces plated with gold to act as lubricants as conventional lubricants evaporate away in the high vacuum conditions of outer space (98).

14.11. Catalyst.

The catalytic properties of gold are under active investigation. Gold has long been used as an alloy with platinum and palladium to act as a diluent to control the activity of these catalytically active elements resulting in an improvement in the selectivity of reaction products (99,100). For example, a gold/palladium catalyst finds commercial use in the production of vinyl acetate (101). Studies show the catalytic activity of gold to be dramatic when in nanoscale particles supported by metal oxides. For example, gold particles of 3 nm deposited on TiO_2 will in the presence of hydrogen provide complete low temperature oxidation of CO and also permit a direct conversion of propylene to propylene peroxide (102).

14.12. Coins and Medallions.

Gold bullion coins minted by national governments have become a convenient, safe way for the public to invest in gold. Government issue gold coins include the American Eagle, Australian Kangaroo, Austrian Philharmoniker, Canadian Maple Leaf, Chinese Panda, United Kingdom Britannia, Mexican Centenario and Libertad, and the South African Kruggerand. Commemorative gold coins that celebrate events, such as the Olympics, are also used as investments. Worldwide fabrication of officially (government) issued coins amounted to over 99 t in 1997, with gold medallions and imitation coins (private issue) consuming an additional 42 t (4,39).

15. Derivatives

15.1. Gold Compounds.

The chemistry of nonmetallic gold is predominantly that of Au(I) and Au(III) compounds and complexes. In the former, coordination number two and linear stereochemistry are most common. The majority of known Au(III) compounds are four coordinate and have square planar configurations. In both of these common oxidation states, gold preferably bonds to large polarizable ligands and, therefore, is termed a class b metal or soft acid.

Although it has been proposed that gold(II) species are intermediate in the reduction of Au(III) to Au(I) chlorides, the only stable mononuclear gold(II) complexes which have been isolated are tetrabutylammonium malenonitriledithiolategold(II) [33637-83-1] (103) and bis(1,4,7-trithiacyclononane)gold(II) bis(tetrafluoroborate) [1254-78-0] (104). Compounds of Au(V) are equally rare. However, both the fluoride, AuF_5 [57542-85-5], and salts of the complex fluoride AuF_6^-, have been prepared (105). Numerous binary and complex gold compounds have been prepared and characterized (106); however, only a few have assumed practical importance. Foremost among these are: the Au(III) halides, which are involved in the purification and analysis of gold as well as being important starting materials for the preparation of other gold compounds, and the alkaline cyanides, which are of importance in the extractive metallurgy and electroplating of the metal.

For the most part, the chemistry of gold is more closely related to that of its horizontal neighbors in the Periodic Table, platinum and mercury, than to the other members of its subgroup, copper and silver. Comprehensive treatments of gold chemistry can be found in the literature (see GENERAL REFERENCES).

Commercially available gold compounds include: $AuBr_3$, $AuCl_3$, $Au(OH)_3$, AuI_3, Au_2O_3, $KAu(CN)_2$, $NaAu(CN)_2$, and Au_2S_3. These are used for the preparation of catalysts, medical compounds, and deposition of gold on surfaces for decoration, electrical/electronics contacts and circuitry, jewelry manufacture, and research. Commercial grade gold cyanides are used for plating of gold and its alloys (4,107).

15.2. Research Potential. Gold compounds remain a fertile field for exploration, for both their medicinal and their industrial potentials. The discoveries of binuclear gold complexes, cluster compounds, and nanoscale particle catalysis are examples of ongoing areas of research. In gold, the relativistic effect of the outer electrons results in many of its exceptional properties, its several colors, and the formation of metallic aurides (37, 108–110). Organogold compounds undergo reactions that provide useful organic compounds or can assist in the production of compounds that cannot be readily obtained in other ways (111,112).

15.3. Halides. Gold(III) chloride [13453-07-1] can be prepared directly from the elements at 200°C (113). It exists as the chlorine-bridged dimer, Au_2Cl_6 in both the solid and gas phases under an atmospheric pressure of chlorine at temperatures below 254°C. Above this temperature in a chlorine atmosphere or at lower temperatures in an inert atmosphere, it decomposes first to AuCl [10294-29-8] and then to gold. The monochloride is only metastable at room temperature and slowly disproportionates to gold(0) and gold(III) chloride. The disproportionation is much more rapid in water both for AuCl and the complex chloride, $[AuCl_2]^-$, formed by interaction with metal chlorides in solution.

The tetrachloroaurate ion, $[AuCl_4]^-$, is most conveniently prepared by dissolving gold in aqua regia. The acid $HAuCl_4$, can be crystallized as the trihydrate by evaporating HCl solutions, whereas the addition of metal halides leads to various salts of the composition $M(AuX_4)_n$. The chlorides in $[AuCl_4]^-$ can be replaced by a variety of charged and neutral ligands. Thus, the tetrabromo- and tetra-cyanoaurates (114) are formed when a solution of the tetrachloroaurate is treated with bromide or cyanide and evaporated. Reaction with fluorine leads to the tetra-fluoroaurates. Similarly, complexes of the type $[AuX_3L]$ can be prepared when L represents nitrogen donors, such as pyridine (115) or nitriles (116). The addition of ammonia leads to the formation of $[Au(NH_3)_4]^{3+}$ (117). Reaction of gold(III) chlorides with easily oxidized ligands such as organophosphines (118), dialkyl-sulfides (119), or mercaptans (120), leads to the corresponding Au(I) complexes, LAuX, which can be oxidized to the corresponding gold(III) complexes with chlorine (121) or converted to other gold(I) complexes, particularly when L is a stabilizing ligand such as a tertiary phosphine.

The chemistry of the bromide is completely analogous to that of the chlorides. Gold(III) iodide [31032-13-0], on the other hand, is unstable, loses iodine, and converts to AuI [10294-31-2] (122).

15.4. Cyanides.

Salts of the complex ion, $[Au(CN)_2]^-$, can be formed directly from gold, ie, gold dissolves in dilute solutions of potassium cyanide in the presence of air. Additionally, a gold anode dissolves in a solution of potassium cyanide. The potassium salt can be isolated by evaporation of the solution and purified by recrystallization from water (123). Boiling of the complex cyanide in hydrochloric acid results in formation of AuCN [506-65-01]. Halogens add oxidatively to $[Au(CN)_2]^-$ to yield salts of $[Au(CN)_2X_2]^-$ which are converted to the tetracyanoaurates using excess cyanide (124). These last can also be prepared directly from the tetrahaloaurates.

15.5. Oxides and Hydroxides.

The existence of Au_2O [1303-57-7] and its hydrated oxides is doubtful. Gold(III) hydroxide [1303-52-2], $Au(OH)_3$, is precipitated from solutions of $(AuCl_4)^-$ by addition of alkali hydroxides. It is dehydrated to the hydrated oxide, Au(O)OH [30779-22-7], and on heating to 140°C, to the oxide Au_2O_3 [1303-58-8] which decomposes to gold and oxygen above 160°C. The hydroxide and hydrated oxide are soluble in both strongly acidic and basic media. In the latter case, salts, eg, $KAuO_2 \cdot 3H_2O$ [12256-44-9], are formed which decompose on heating.

15.6. Sulfides.

Gold(I) sulfide [30695-60-4], Au_2S, is formed when acidified solutions of $KAu(CN)_2$ are treated with H_2S. It is highly insoluble in water and dilute acids but reacts with strong oxidizing agents, such as aqua regia or chlorine, or with strongly complexing anions such as cyanide. The less stable Au_2S_3 [1303-61-3] can be prepared from $AuCl_3$ or complex chloraurates by reaction with hydrogen sulfide in anhydrous ether. The reaction in aqueous solutions leads to formation of metallic gold as does heating of the compound in air.

15.7. Organogold Compounds.

Both alkyl and aryl complexes of Au(I) and Au(III) as well as olefin and acetylene complexes have been prepared and studied. In general, the preparation of alkyls and aryls involves the reaction of a gold halide with a Grignard or organolithium reagent; halides can be displaced directly by unsaturated hydrocarbons. Stabilization of the σ-bonded compounds of Au(I) is facilitated by the presence of donor ligands such as tertiary phosphines or arsines. For example, complexes of the type, R_3PAuCH_3, are prepared by the reaction of R_3PAuCl and CH_3Li (125). Addition of a second mole of CH_3Li leads to formation of $Li(Au(CH_3)_2$ [53863-37-9] (126) which decomposes when recovery from diethyl ether solution is attempted, but can be isolated as a stable adduct of $(CH_3)_2NCH_2CH_2N(CH_3)CH_2CH_2N(CH_3)_2$ (127). The alkyl tertiary phosphine gold(I) complexes decompose thermally to gold(0) and a dimer of the alkyl. Thus, heating of R_3PAuCH_3 to 100°C leads to formation of ethane (128). Reaction with acids cleaves the gold—carbon bond with formation of hydrocarbon, eg, CH_4 in the case of R_3PAuCH_3 (125), whereas halogens react to yield alkyl halides and the corresponding Au(I) or Au(III) halides (129). Reaction with Hg(II) salts leads to exchange of the alkyl group for halide (130). Addition of methyl iodide leads initially to formation of the dimethylgold(III) complex which reacts rapidly with more R_3PAuCH_3 to yield $R_3PAu(CH_3)_3$. This, in turn, reacts more slowly to yield ethane (131).

Dialkylgold(III) halides are prepared by the reaction of a Grignard reagent with a gold(III) halide (131). They are readily converted to other dimethylgold(III) complexes via reaction with the appropriate silver salt, eg, AgCN (132), or by replacement of the halide with a donor ligand (133). Dialkylgold(III) halides are inert to acids and metal halides and react slowly with halogens (134). Trialkyl-gold(III) complexes can be prepared from Au(III) halides by reaction with alkyllithium reagents, but these compounds are unstable unless a donor ligand also is added. The stable compounds are prepared more conveniently by treating the appropriate Au(I) halide with alkyllithium and methyl iodide (135). The tetramethylgold(III) anion can be prepared and stabilized in the same way as described for the dimethylgold(I) anion (127). The tri- and tetraalkylgold(III) complexes react with acids, halogens, and metal halides to yield the dialkyl species.

Olefin and acetylene complexes of Au(I) can be prepared by direct interaction of the unsaturated compounds with a Au(I) halide (136,137). The resulting products, however, are not very stable and decompose at low temperatures. Reaction with Au(III) halides leads to halogenation of the unsaturated compound and formation of Au(I) complexes or polynuclear complexes with gold in mixed oxidation states.

15.8. Cluster Compounds. More recently, an increasing amount of interest has developed in gold-containing bimetallic cluster compounds (138) which permit investigation at the molecular level of the metal—metal interactions thought to occur in bimetallic catalysts or alloys. Most often, these compounds are prepared from organophosphine stabilized Au(I) compounds such as halides or alkyls and generally contain one to three gold phosphine fragments bonded to one or more transition metal atoms, most often as carbonyl species.

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