

**ENCYCLOPEDIA
OF INDUSTRIAL
CHEMICAL
ANALYSIS**

VOLUME 16

**Mercury
to
Penicillins**

ENCYCLOPEDIA OF INDUSTRIAL CHEMICAL ANALYSIS

Edited by Foster Dee Snell and Leslie S. Ettre

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**Mercury
to
Penicillins**

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VOLUME 16

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ABBREVIATIONS AND SYMBOLS

A	ampere(s)	B	bel(s)
Å	Angstrom unit(s)	b	barn(s)
AATCC	American Association of Textile Chemists and Colorists	b (as in b_{11})	boiling (at 11 torr)
ac	alternating current	bbl	barrel(s)
Ac	acetate, acetyl (in formulas)	Bé	Baumé
ACS	American Chemical Society	beV	billion electron volt(s)
AIChE	American Institute of Chemical Engineers	Bhn	Brineil hardness number
AIP	American Institute of Physics	bp	boiling point
ANSI	American National Standards Institute, Inc.	BP	<i>British Pharmacopeia</i>
AOAC	Association of Official Analytical (formerly Agricultural) Chemists	BS	British Standards
APHA	American Public Health Association	Btu	British thermal unit(s)
API	American Petroleum Institute	C	centigrade; Celsius; coulomb(s)
approx	approximately	C-	denoting attachment to carbon (eg, C-acetyl- indoline)
ar-	aromatic (eg, ar-vinyl- aniline)	cal	calorie(s); gram calorie(s)
as-	asymmetric(al) (eg, as- trichlorobenzene)	calcd	calculated
ASA	American Standards Association (now American National Standards Institute, Inc., ANSI)	cg	centigram(s)
ASTM	American Society for Testing and Materials	cgs	centimeter-gram-second
atm	atmosphere(s)	Ci	curie(s)
at. no.	atomic number	CI	Colour Index
ATR	attenuated total reflectance	cm	centimeter(s)
at. wt	atomic weight	cp	chemically pure
av	average	cP	centipoise(s)
		cps	cycles per second
		cSt	centistokes
		cu	cubic
		d	density
		d-	<i>dextro</i> -, dextrorotatory
		D-	denoting configurational relationship (related to <i>dextro</i> -glyceraldehyde)
		D	Debye unit(s)
		dB	decibel(s)
		dc	direct current
		dec	decomposes
		dec pt	decomposition point
		dl-, DL-	racemic
		DOT	Dept. of Transportation (U.S.)

dp	dew point	ID	inner diameter
DP	degree of polymerisation	in.	inch(es)
DS	degree of substitution	insol	insoluble
DTA	differential thermal analysis	IP	<i>International Pharmacopeia</i>
dyn	dyne(s)	IR	infrared
e	electron(s)	ISO	International Organization for Standardisation
ed.	edition(s); editor(s)		
emf	electromotive force		
emu	electromagnetic unit(s)	IU	international units
eq	equivalent(s)	IUPAC	International Union of Pure and Applied Chemistry
estd	estimated		
esu	electrostatic unit(s)	J	joule(s)
Et	ethyl (in formulas)	K	Kelvin
eV	electron volt(s)	kc	kilocycle(s)
exptl	experimental	kcal	kilogram-calorie(s)
F	Fahrenheit; farad(s)	keV	kiloelectron volt(s)
FCC	<i>Food Chemicals Codex</i>	kg	kilogram(s)
FDA	U.S. Food and Drug Administration	km	kilometer(s)
fl oz	fluid ounce(s)	kV	kilovolt(s)
FMIR	frustrated multiple internal reflectance	kW	kilowatt(s)
fob	free on board	kWh	kilowatt-hour(s)
fp	freezing point	l	liter(s)
ft	foot (feet)	l-	<i>levo-</i> , levorotatory
ft-lb	foot-pound(s)	L-	denoting configurational relationship (related to <i>levo</i> -glyceraldehyde)
g	gram(s)		
G	gauss	lb	pound(s)
gal	gallon(s)	LD ₅₀	dose lethal to 50% of the animals tested
GC	gas chromatography	lm	lumen(s)
gem-	geminal (attached to the same atom)	ln	logarithm (natural)
GLC	gas-liquid chromatography	log (instead of log ₁₀)	logarithm (common)
g-mol	gram molecular (as in g-mol wt)	m	meter(s)
g-mole	gram-mole(s)	m-	meta (eg, <i>m</i> -xylene)
hp	horsepower	M	molar
hr	hour(s)	mA	milliampere(s)
Hz	Hertz	mAh	milliampere-hour(s)
i-	inactive (eg, <i>i</i> -methionine)	max	maximum
ibp	initial boiling point	Mc	megacycle(s)
ICC	Interstate Commerce Commission	MCA	Manufacturing Chemists' Association
ICT	International Critical Tables	Me	metal or methyl (in formulas)
		meq	milliequivalent(s)
		MeV	million electron volt(s)

mg	milligram(s)	ppb	parts per billion (1/10 ⁹)
mil	0.001 inch	ppm	parts per million (1/10 ⁶)
min	minute(s); minimum	pptd	precipitated
ml	milliliter(s)	psi	pound(s) per square inch
mm	millimeter(s)	psia	pound(s) per square inch absolute
mμ	millimicron(s)	psig	pound(s) per square inch gage
mM	millimole(s)	r	Roentgen
mo	month(s)	R	alkyl group
mol wt	molecular weight	R _r	retardation factor (chromatography)
mp	melting point	rh	relative humidity
mph	miles per hour	rpm	revolutions per minute
MS	mass spectrometry, mass spectrometer; molar substitution	rps	revolutions per second
<i>n</i> (as <i>n</i> _D ²⁰)	index of refraction (for 20°C and sodium D line)	S-	denoting attachment to sulfur (eg, <i>S</i> -methyl- cysteine)
<i>n</i> -	normal (eg, <i>n</i> -butyl)	sec	second(s)
<i>N</i>	normal as applied to concentration	sec-	secondary (eg, <i>sec</i> -butyl)
<i>N</i> -	denoting attachment to nitrogen (eg, <i>N</i> - methylaniline)	sl sol	slightly soluble
NBS	National Bureau of Standards	sol	soluble
ND	<i>New Drugs</i> (formerly <i>New and Nonofficial Drugs</i>) (American Medical Association)	soln	solution
NF	<i>National Formulary</i> (American Pharma- ceutical Association)	sp gr	specific gravity
NMR	nuclear magnetic reson- ance	sq	square
no.	number	St	stokes
<i>o</i> -	ortho (eg, <i>o</i> -xylene)	STP	standard temperature and pressure (760 torr and 0°C)
<i>O</i> -	denoting attachment to oxygen (eg, <i>O</i> -acetyl- amine)	subl	sublimes
OD	outer diameter	<i>sym</i> -	symmetrical (eg, <i>sym</i> - dichloroethylene)
Oe	oersted(s)	<i>t</i> -, <i>tert</i> -	tertiary (eg, <i>t</i> -butyl)
oz	ounce(s)	TAPPI	Technical Association of the Pulp and Paper Industry
<i>p</i> -	para (eg, <i>p</i> -xylene)	temp	temperature
P	poise(s)	<i>tert</i> -, <i>t</i> -	tertiary (eg, <i>tert</i> -butyl)
Ph	phenyl (in formulas)	TLC	thin-layer chromatog- raphy
PMMA	poly(methyl meth- acrylate)	torr	Toricelli (mm Hg)
		Twad	Twaddell
		USASI	United States of America Standards Institute (now American National Standards Institute, Inc., ANSI)

USP	(The) <i>United States Pharmacopeia</i> (Mack Publishing Co., Easton, Pa.)	wt	weight
		w/v	weight per volume
		w/w	weight per weight
UV	ultraviolet	X	halogen (in formulas)
V	volt(s)	yd	yard(s)
vic-	vicinal (attached to adjacent atoms)	yr	year(s)
		μ	micron(s)
vol	volume	μ g	microgram(s)
vs	versus	μ l	microliter(s)
v sol	very soluble	μ m	micrometer(s)
v/v	volumes per volume	μ M	micromole
W	watt(s)	Ω	ohm(s)
Wh	watt-hour(s)	Ω -cm	ohm-centimeter(s)

Prefixes Indicating Order of Magnitude

c	deci (10^{-1})	h	hecto (10^2)
d	centi (10^{-2})	k	kilo (10^3)
m	milli (10^{-3})	M	mega (10^6)
μ	micro (10^{-6})	G	giga (10^9)
n	nano (10^{-9})	T	tera (10^{12})
p	pico (10^{-12})		
f	femto (10^{-15})		
a	atto (10^{-18})		

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Mercury, Hg, atomic number 80, atomic weight 200.59 ± 0.03 (9), is the only metal that is liquid at room temperatures. Below its melting point of -38.67°C it is a white solid and above its boiling point of 356.9°C , a colorless monatomic vapor. The symbol Hg derives from Greek *hydrargyros* or Latin *hydrargyrum*, "silver water" or "liquid silver." It is the third and last member of Group IIb of the Periodic System; the other two are zinc and cadmium. Although zinc and cadmium show many similarities and are often discussed together, mercury differs in so many aspects of its properties and behavior that it is in a class by itself.

Mercury occurs in the lithosphere to the extent of about $5 \times 10^{-5}\%$, or 0.5 g/metric ton; about the same as selenium and iodine and half as abundant as zinc (10). As listed in Table 1, it possesses seven natural, and 15 radioactive isotopes (1,10).

Mercury and its most important ore, cinnabar, HgS, have been known since antiquity. Aristotle mentions its use in religious rites; the Almaden mine in Spain was described by Theophrastus. It was early used in medicinal preparations; its use in the treatment of syphilis was introduced by Paracelsus in the sixteenth century.

For details on the properties, occurrence, and manufacturing of mercury and its compounds, the general references (1-8) should be consulted.

Sources. There are few mercury minerals, and practically the only one of commercial significance is cinnabar: mercuric sulfide, HgS. Occasionally small amounts of native mercury are found associated with cinnabar and metacinnabar, a sulfide in which some of the mercury has been replaced by iron or zinc, but there are no exploitable deposits of either native mercury or metacinnabar. There exist minor deposits of calomel, Hg_2Cl_2 , and Tiemannite, HgSe; and small amounts of mercury are recovered as a by-product of zinc extraction.

In approximate order of importance, the world's production of mercury comes from Spain, Italy, the Soviet Union, United States of America, Mexico, Canada, the People's Republic of China, and Yugoslavia. Many other countries produce lesser amounts. The Almaden mine in Spain has been in production continuously since Greco-Roman times. Production figures for the years 1967-1969 are cited in Table 2 (11). The unit used, flasks, which is unique to mercury, is equivalent to 76 lb or 34.5

2 MERCURY

Table 1. Isotopes of Mercury

Mass number	Abundance, %	Half life
<192		ca 3 hr
<195		42 sec
189		25 min
190		90 min
191		57 min
192		6 hr
193 ^m		12 hr
193		5 hr
194 ^m		0.4 sec
195 ^m		40 hr
195		9.5 hr
196	0.146	
197 ^m		25 hr
198	10.02	
199 ^m		43 min
199	16.84	
200	23.13	
201	13.22	
202	29.80	
203		48 day
204	6.85	
205		5.2 min

Table 2. World Production of Mercury, by Countries, in Flasks^a

Country	1967	1968	1969
Bolivia	100	134	68
Canada ^b		5000	20,000
Chile	184	513	275
People's Republic of China ^b	20,000	20,000	20,000
Colombia	210	362	344
Czechoslovakia	203	116	150
Ireland			420
Italy	48,066	52,215	48,733
Japan	4617	5084	5599
Mexico ^c	14,417	17,202	22,500
Peru	3315	3119	3360
Phillippines	2611	3544	3478
Rumania	190	203 ^b	200 ^b
Soviet Union ^b	45,000	45,000	47,000
Spain	49,227	57,262	64,406
Tunisia	292	309	320
Turkey	4147	4320	4800
United States of America	23,784	28,874	29,360
Yugoslavia	15,890	14,794	14,330
Total ^d	232,073	258,051	285,343

^a 1 flask = 76 lb = 34.5 kg.

^b Estimated.

^c Official figures as reported by government bureau; production believed to be much higher.

^d Total is of listed figures only, does not include production of other countries not listed.

kg; this strange unit originated in the Spanish mines during workings by the Romans who used a weight of 75 *librae*. One *libra* = 1.014 lb, so 75 *librae* = 76.05 lb; by international agreement the fraction was dropped.

Secondary mercury, recovered from primary uses, is an important factor in the United States supply, representing about 20% of domestic requirements. If properly purified it is equal in every respect to primary metal.

As shown in Table 2, total world production in 1969 was about 21.5 million lb, or 10,000 short tons of mercury.

Properties

Some physical and electrochemical properties of mercury are listed in Table 3 (1). The metal owes its scientific and industrial importance to some of these properties: it has a uniform volume expansion over its entire liquid range, which, taken together with its high surface tension and its consequent inability to wet and cling to glass, makes it useful in barometers, thermometers, manometers, and other measuring devices. The liquidity of mercury at ordinary temperatures enhances its usefulness for these purposes. The low electrical resistivity is made use of in many electrical contact applications. Mercury has the high thermal neutron cross section of 363 barns, enabling it to absorb neutrons and act as a shield for atomic devices, while its high thermal conductivity permits it to act as a coolant and makes it useful in boilers.

Mercury is the most fusible of all metals and its volatility is unparalleled among metals. The only others that boil below 1000°C are the alkali metals, cadmium, and zinc. The comparison shown in Table 4 emphasizes its uniqueness.

One m³ of air saturated at 20°C contains 14 mg, and at 100°C 2.4 g, of mercury. The vapor is practically entirely monatomic; thus, except for the inert gases, mercury is the only element that gives a significant concentration of a monatomic vapor at

Table 3. Properties of Mercury

melting point, °C	-38.87
boiling point, °C	356.9
atomic distance, Å	3.05
thermal conductivity, (cal)/(sec)(cm ²)(°C/cm)	0.022
critical pressure, atm	732
critical temperature, °C	1677
density, g/cm ³ , at 20°C	13.546
at mp	14.43
at -38.8°C (solid)	14.193
electrode potentials, normal, V	
$\text{Hg}^{2+} + 2\text{e}^- = \text{Hg}$	0.851
$\text{Hg}_2^{2+} + 2\text{e}^- = 2\text{Hg}$	0.7961
$2\text{Hg}^{2+} + 2\text{e}^- = \text{Hg}_2^{2+}$	0.905
expansion coefficient (vol) liquid, 20°C, per °C	182×10^{-4}
latent heat of fusion, cal/g	2.82
latent heat of vaporization, cal/g	65
hydrogen overvoltage, V	1.06
ionization potentials, V	
first	10.43
second	18.75
third	34.30
resistivity, ohm-cm, at 20°C	95.8×10^{-4}
solubility in water, µg/liter	20-30

Table 4. Vapor Pressure of Some Group II Elements

Element	Vapor pressure, torr	
	200°C	600°C
magnesium	$\approx 10^{-6}$	7
zinc	2×10^{-5}	12
cadmium	3×10^{-4}	80
mercury	18	16,500 (= 22 atm)

moderate temperatures (5). It resembles the inert gases in some other respects, such as its solubility in water. Its electronic configuration is $4f^{14}5d^{10}6s^2$, and the resemblance to an inert gas is in part attributed to the phenomenon of the "inert pair" of electrons, in which the two outer electrons—the 6s in the case of mercury—behave as if they formed a complete shell instead of as valency electrons. Examples of this behavior, in addition to mercury, include many of the heavier elements. For example, indium and thallium may have a valence of 1 as well as of 3; tin and lead may have a valence of 2 as well as 4. On the other hand, if the two valency electrons of mercury become "inert" the element is left with zero valency, like an inert gas.

Electrochemically, mercury is relatively noble, as indicated by the electrode potentials in Table 3; this property distinguishes it sharply from the other two members of Group IIB, zinc and cadmium. Its propensity to form alloys, the so-called amalgams, with almost all metals, coupled with its high hydrogen overvoltage of over 1 V, make possible the electrodeposition on a mercury cathode of many metals which would not otherwise be depositable from aqueous solution; this accounts for its major industrial use in the production of caustic soda and potash, as well as the analytical technique of polarography, the "dropping mercury electrode" (see Vol. 1, pp. 161–199).

The only metals having little tendency to alloy, or amalgamate, with mercury are iron, niobium, vanadium, molybdenum, tantalum, and tungsten. The inertness of iron is utilized in the packaging of mercury commercially in iron flasks; but even iron reacts at high temperatures.

At ordinary temperatures mercury is stable and does not react with air, ammonia, carbon dioxide, nitrous oxide, or oxygen. At somewhat elevated temperatures it reacts with air or oxygen to form mercuric oxide, which decomposes back to the element if the temperature is raised still further. It combines readily with the halogens and sulfur; it is little affected by hydrochloric and dilute sulfuric acid, but is attacked by concentrated sulfuric acid. Dilute or concentrated nitric acid reacts with mercury, forming mercurous salts when the mercury is in excess in the cold, and mercuric salts when the acid is in excess or the temperature is raised.

The tendency of many metals to amalgamate with mercury has been mentioned; that at least some of these amalgams consist of actual compounds rather than simply

Table 5. Melting Points of Alkali Metals and Their Amalgams

Metal	mp of pure metal, °C	Formula of amalgam	mp of amalgam, °C
sodium	98	Hg_2Na	346
potassium	64	Hg_2K	270
mercury	–39		

solutions is shown by their melting points, which may be much higher than those of the components. Table 5 (5) illustrates this for the sodium and potassium amalgams.

Mercury is divalent in virtually all of its compounds. Its monovalency in the mercurous compounds is only apparent, because the evidence is overwhelming that mercurous chloride, eg, is not HgCl but Hg_2Cl_2 , formulated as Cl-Hg-Hg-Cl (4,5). It seems preferable, therefore, to retain the nomenclature mercurous/mercuric rather than mercury(I) and mercury(II). This tendency of mercury to form links with itself serves further to distinguish it from the other metals of Group II, although cadmium shows some slight evidence of such behavior. Still further manifestations of the uniqueness of mercury are provided by the coordinate rather than ionic nature of many of the mercuric salts: mercuric chloride, HgCl_2 , is practically nonionized in aqueous solution.

The relationships between mercury metal, mercurous compounds, and mercuric compounds have important bearing on the analytical chemistry of the element. The relevant thermodynamic values are listed in Table 6 (4).

Table 6. Equilibrium Potentials of the Oxidation States of Mercury

Reaction	E^0 , V
$\text{Hg}_2^{2+} + 2e = 2 \text{Hg} (l)$	0.789
$2 \text{Hg}_2^{2+} + 2e = \text{Hg}_3^{2+}$	0.920
$\text{Hg}_2^{2+} + 2e = \text{Hg}_2^+ (l)$	0.854
$\text{Hg}_2^{2+} = \text{Hg} (l) + \text{Hg}^{2+}$	-0.131

As given in the last equation in Table 6, E^0 for the disproportionation equilibrium is -0.131 V; for the same equation

$$K = \frac{[\text{Hg}_2^{2+}]}{[\text{Hg}_2^{2+}]} = 6.0 \times 10^{-3}$$

The potentials show that only oxidizing agents with potentials in the range -0.79 to -0.85 V will oxidize mercury to Hg_2^{2+} but not to Hg^{2+} . Few oxidizing agents meet this requirement, so that when mercury is treated with an excess of oxidizing agent it is converted entirely to Hg_2^{2+} . When, however, mercury is in at least 50% excess only Hg_2^{2+} is obtained because, as given by the last equation of Table 6, $\text{Hg} (l)$ easily reduces Hg_2^{2+} to Hg_2^{2+} .

The equilibrium constant $K = 6 \times 10^{-3}$, shows that although Hg_2^{2+} is stable with respect to disproportionation, it is so only by a small margin. Thus any reagent that reduces the activity, by precipitation or complexation, of Hg_2^{2+} to a significantly greater extent than it lowers the activity of Hg_2^{2+} will cause the Hg_2^{2+} to disproportionate. Since there are many such reagents, the number of stable mercurous compounds is rather small. Thus on adding OH^- to a mercurous solution a dark precipitate consisting of mercury and HgO is formed. Similarly, addition of sulfide ions to a mercurous solution gives a mixture of mercury and the extremely insoluble HgS . Mercurous cyanide does not exist because although $\text{Hg}(\text{CN})_2$ is soluble it is very slightly dissociated (4).

For analogous reasons, although mercuric ion is easily reduced to mercurous, most reagents cause reduction all the way to metal. With phosphorous acid the reduction can be terminated at the mercurous stage if the temperature is kept below 60°C and