BROMINE

1. Introduction

Bromine, Br_2, [7726-95-6], is the only nonmetallic element that is a liquid at standard conditions. The Bromine (Br) atom [10097-32-2] has at no. 35, at wt 79.904, and belongs to Group 17 (VIIA) of the Periodic Table, the halogens. Its electronic configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^5$. The element's known isotopes range in mass number from 74 to 90. Isotopes usable as radioactive tracers are 77, 80, 80m (metastable), and 82. Bromine has two stable isotopes, ^{79}Br and ^{81}Br. The most common valence states are -1 and $+5$, but $+1$, $+3$, and $+7$ are also observed. The covalent radius of bromine is 0.1193 nm. The ionic radius of the bromide ion [24959-67-9], is 0.197 nm and of Br(VII) Br^{+7}, [20681-12-3] is 0.039 nm. The name bromine is derived from the Greek word, *bromos,* meaning stench.

Bromine occurs in the hydrosphere mainly as soluble bromide salts. Its concentration ranges from 65 mg/L in seawater up to 6.5 g/L in the southern basin of the Dead Sea. In 1826, Antoine-Jerome Balard in France published the discovery of bromine, which was isolated by chlorinating seawater bitterns and distilling out bromine. Bromine had been prepared earlier by Joss and Liebig but neither of them recognized it as an element (1). Around 1840 bromine was used in photography. The first mineral to contain bromine was apparently silver bromide, discovered in 1941 by Berthier. Its first medical use was in 1857 when bromides were used for the treatment of epilepsy. The first commercial bromine production from salt brines was in 1846 at Freeport, Pennsylvania. In 1858, potash was discovered in the Stassfurt salt deposits in Germany and bromine was a by-product from the potash production. Herbert Dow invented the "blowing out" process for Midland (Michigan) brines in 1889. The antiknock properties of tetraethyllead, $(CH_3CH_2)_4Pb$, [78-00-2] were discovered in 1921 and soon after ethylene dibromide, $C_2H_4Br_2$, [106-93-4] was found to aid the removal of lead from combustion chambers. At one time, ~80% of all bromine was used to produce ethylene dibromide. Bromine was first commercially extracted from seawater in 1934, using the Dow process. The richest source of Br in the world is found in the Dead Sea brines, which contain up to 12 g/L of Br^-. Its commercial exploitation by DSBG started in 1957. In the 1950s, bromine was discovered in south Arkansas brines, the only significant source of bromine in the United States, with a bromine content of 2–5 g/L (see CHEMICALS FROM BRINE).

2. Physical Properties

Bromine is a dense, dark red, mobile liquid that vaporizes readily at room temperature to give a red vapor that is highly corrosive to many materials and human tissues. Bromine liquid and vapor, up to ~600°C, are diatomic (Br_2). Table 1 summarizes the physical properties of bromine.

Remark: While bromine does not form a true azeotrope with water, bromine saturated with water or mixed with it creates a solution that boils at 54.3°C, compared with 58.8°C for dry bromine. The distillate contains ~2% water.

Table 1. **Physical Properties of Bromine**[a]

Property	Value
stable isotope abundance, %	
^{79}Br	50.54%
^{81}Br	49.46%
mol wt	159.808
freezing point, °C	−7.25
bp, °C	58.8
density, g/mL	
15°C	3.1396
20°C	3.1226
25°C	3.1055
30°C	3.0879
vapor density, g/L, 0°C, 101.3 kPa[b]	7.139
refractive index	
20°C	1.6083
25°C	1.6475
viscosity,mm^2/s (=cSt)	
20°C	3.14×10^{-1}
30°C	2.88×10^{-1}
40°C	2.64×10^{-1}
50°C	2.45×10^{-1}
surface tension,mN/m (=dyn/cm), 25°C	40.9
solubility parameter, 25°C,$(J/cm^3)^{1/2}$[c]	23.5
critical temperature, °C	311
critical pressure, MPa[d]	10.3
thermal conductivity,$W/(m \cdot K)$	0.123
specific conductivity,$(\Omega \cdot cm)^{-1}$	9.10×10^{-12}
dielectric constant, 25°C, 10^5 Hz	3.33
electrical resistivity, 25°C, $\Omega \cdot cm$	6.5×10^{10}
expansion coefficient from 20–30°C, per °C	0.0011
compressibility, 20°C from 0–10 MPa[d]	62.5×10^{-6}
heat of vaporization, 50°C, J/g[c]	187
heat of fusion,−7.25°C, J/g[c]	66.11
heat capacity, J/mol[c]	
15 K	7.217
30 K	22.443
60 K	36.33
240 K	57.94
265.9 K	61.64
265.9 K[e]	77.735
288.15 K[f]	78.66
electronegativity	3.0
electron affinity, kJ[c]	330.5

[a] References 2–5.
[b] To convert kPa to mmHg, multiply by 7.50.
[c] To convert J to cal, divide by 4.184.
[d] To convert MPa to bar, multiply by 10.
[e] Solid bromine.
[f] Liquid bromine.

Bromine is moderately soluble in water, 33.6 g/L at 25°C. It gives a crystalline hydrate having a formula of $\sim Br_2 \leq 7.9H_2O$ (6). The solubilities of bromine in water at several temperatures are given in Table 2. Aqueous bromine solubility increases in the presence of bromides or chlorides because of complex ion

Table 2. **Aqueous Solubility of Bromine**[a]

Temperature, °C	Solubility, g/100 g soln	Temperature, °C	Solubility, g/100 g soln
0	2.31 (4.05)[b]	20	3.41
3	3.08 (3.85)[b]	25	3.35
5	3.54 (3.77)[b]	40	3.33
10	3.60	53.6[c]	3.50

[a] References 7–9.

[b] These solutions are metastable.

[c] This is the boiling point.

formation. This increase in the presence of bromides is illustrated in Figure 1. Equilibrium constants for the formation of the tribromide and pentabromide ions at 25°C have been reported (11).

$$\mathrm{Br_2 + Br^-} \rightleftharpoons \mathrm{Br_3^-} \qquad K = 16.85\ M^{-1}$$

$$\mathrm{Br_3^- + Br_2} \rightleftharpoons \mathrm{Br_5^-} \qquad K = 1.45\ M^{-1}$$

Bromine is soluble in nonpolar solvents and in certain polar solvents such as alcohol and sulfuric acid. It is miscible with alcohol, ether, carbon disulfide, and many halogenated solvents. Bromine reacts with some of these solvents under certain conditions.

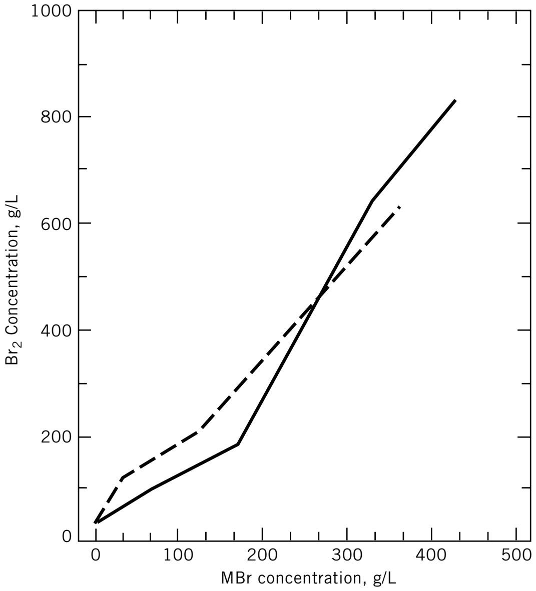


Fig. 1. Solubility of bromine in the presence of (—) NaBr and (– – –) KBr (10).

Bromine can function as a solvent. One of the very few metal bromides that has significant solubility in bromine is cesium bromide, 19.3 g/100 g of solution, thus providing a method of separating cesium bromide from the other alkali bromides (12). Aluminum bromide also is reported to have significant solubility in bromine but the published solubility values are not in good agreement (13). Bromine serves as the solvent in some brominations of organic compounds, such as 1,2-diphenylethane (14).

3. Chemical Properties

One of the central features of the chemistry of the halogens is the tendency to acquire an electron to form either a negative ion, X^-, or a single covalent bond, $-X$, and bromine is no exception. The halogens are electron rich systems having few potential bonding orbitals. Except for helium and neon, all of the elements in the Periodic Table form halides with one or more of the halogens. Halides that are predominately ionic tend to have high conductivities when fused, high boiling points, and if soluble in water, are generally not hydrolyzed. Predominately covalent halides are volatile, nonconductive in the liquid state, and usually readily hydrolyzed (15).

Nonmetal halides are generally hydrolyzed to a hydrogen halide and to an oxy-acid containing the other element. The first row nonmetal halides, eg, CCl_4, resist hydrolysis because the nonmetal element cannot expand its octet of electrons to form a bond to water before its bond to the halide is broken. Hydrolysis requires either an energetic water molecule to strike the halide or ionization of the covalent nonmetal–halide bond, processes that tend to be quite slow (16).

3.1. Reaction with Hydrogen and Metals.

Bromine combines directly with hydrogen at elevated temperatures and this is the basis for the commercial production of hydrogen bromide [10036-10-6]. Heated charcoal and finely divided platinum metals are catalysts for the reaction (17).

Bromine reacts with essentially all metals, except tantalum and niobium, although elevated temperatures are sometimes required, eg, solid sodium does not react with dry bromine but sodium vapor reacts vigorously. Metals such as lead, magnesium, nickel, and silver react with bromine to form a surface coat of bromide that resists further attack. This protective coating allows lead and nickel to be used as linings in bromine containers. Metals tend to be corroded by bromine faster in the presence of moisture than without, probably because of the formation of hydrobromic and hypobromous acids.

Bromine reacts with some metal oxides, eg, thorium oxide, at high temperatures in the presence of reducing agents to form bromides (18). Certain nonhydrated metal halides can be formed by precipitation. These include AgBr, CuBr, AuBr, TlBr, $PbBr_2$, $PtBr_2$, and Hg_2Br_2 (19).

3.2. Reaction with Other Halides.

Bromide ion is oxidized by chlorine to bromine, which is the basic reaction in the production of bromine from brines, seawater, bitterns, or bromine containing wastes.

$$2\,Br^- + Cl_2 \longrightarrow Br_2 + 2\,Cl^-$$

Iodide ion is oxidized by bromine to iodine.

$$2\,I^- + Br_2 \longrightarrow I_2 + 2\,Br^-$$

Among the interhalogen compounds containing bromine are BrF, BrF_3, BrF_5, BrCl, and IBr. Bromine is soluble in chlorine in all proportions, yielding an equilibrium mixture of the interhalogen bromine chloride:

$$Br_2 + Cl_2 \rightarrow 2BrCl \qquad K_{eq} = 2.94\ at\ 25°C$$

This equilibrium mixture can be separated by distillation.

The interhalogens are characterized by great reactivity. The higher fluorides are quite thermally stable. Bromine pentafluoride [7789-30-2], BrF_5, which is stable up to 460°C, is the most reactive of the higher fluorides and reacts with all of the elements except nitrogen, oxygen, and the noble gases (15). Solid polyhalide salts are known. Examples are NH_4IBr_2, $RbBrCl_2$, and KClIBr (20).

3.3. Reaction with Nonmetals. Bromine oxidizes sulfur and a number of its compounds.

$$H_2S + Br_2 \longrightarrow S + 2\,HBr$$

$$S + 3\,Br_2 + 4\,H_2O \longrightarrow H_2SO_4 + 6\,HBr$$

$$SO_2 + Br_2 + 2\,H_2O \longrightarrow 2\,HBr + H_2SO_4$$

$$Na_2S + 4\,Br_2 + 8\,NaOH \longrightarrow Na_2SO_4 + 8\,NaBr + 4\,H_2O$$

Bromine also oxides red phosphorus and some phosphorus compounds.

$$2\,P + 3\,Br_2 + 6\,H_2O \longrightarrow 6\,HBr + 2\,H_3PO_3$$

$$H_3PO_3 + Br_2 + H_2O \longrightarrow H_3PO_4 + 2\,HBr$$

$$H_3PO_3 + Br_2 + 3\,NaOH \longrightarrow NaH_2PO_4 + 2\,NaBr + 2\,H_2O$$

Ammonia, hydrazine, nitrites, and azides are oxidized by bromine. Nitrogen is often a product of such reactions.

$$2\,NH_3 + 3\,Br_2 + 6\,NaOH \longrightarrow 6\,NaBr + N_2\uparrow + 6\,H_2O$$

$$8\,NH_4OH + 3\,Br_2 \longrightarrow 6\,NH_4Br + N_2\uparrow + 8\,H_2O$$

$$N_2H_4 + 2\,Br_2 + 4\,NaOH \longrightarrow 4\,NaBr + N_2\uparrow + 4\,H_2O$$

$$NaNO_2 + Br_2 + H_2O \longrightarrow NaNO_3 + 2\,HBr$$

Under certain circumstances bromine reacts with ammonia and amino compounds to form bromamide, NH_2Br, [14519-10-9] bromimide, $NHBr_2$, [14519-03-0], or nitrogen bromide, NBr_3, [15162-90-0]. These compounds can decompose explosively so great care should be exercised any time bromine and ammonia or amino compounds might come in contact with each other (see BROMINE INORGANIC COMPOUNDS).

Bromine oxidizes carbon and reacts with carbon monoxide to form carbonyl bromide [593-95-3].

$$C + Br_2 + H_2O \longrightarrow 2\ HBr + CO\uparrow$$

$$Br_2 + CO \longrightarrow COBr_2$$

3.4. Reactions in Water. The ionization potential for bromine is 11.8 eV and the electron affinity is 3.78 eV. The heat of dissociation of the Br_2 molecule is 192 kJ (46 kcal). The reduction potentials for bromine and oxybromide anions in aqueous acid solutions at 25°C are(21)

$$Br_2(aq) + 2\ e^- \longrightarrow 2\ Br^- \qquad E^\circ = +1.0873\ V$$

$$Br_2(l) + 2\ e^- \longrightarrow 2\ Br^- \qquad E^\circ = +1.066\ V$$

$$HOBr + H^+ + 2\ e^- \longrightarrow Br^- + H_2O \qquad E^\circ = +1.331\ V$$

$$HOBr + H^+ + e^- \longrightarrow \tfrac{1}{2}Br_2(aq) + H_2O \qquad E^\circ = +1.574\ V$$

$$HOBr + H^+ + e^- \longrightarrow \tfrac{1}{2}Br_2(l) + H_2O \qquad E^\circ = +1.596\ V$$

$$BrO^- + H_2O + 2\ e^- \longrightarrow Br^- + 2\ OH^- \qquad E^\circ = +0.761\ V$$

$$BrO_3^- + 6\ H^+ + 5\ e^- \longrightarrow \tfrac{1}{2}Br_2 + 3\ H_2O \qquad E^\circ = +1.482\ V$$

$$BrO_3^- + 6\ H^+ + 6\ e^- \longrightarrow Br^- + 3\ H_2O \qquad E^\circ = +1.423\ V$$

$$BrO_3^- + 3\ H_2O + 6\ e^- \longrightarrow Br^- + 6\ OH^- \qquad E^\circ = +0.61\ V$$

When bromine dissolves in water, it partially disproportionates.

$$Br_2 + H_2O \rightleftarrows HOBr + H^+ + Br^-$$

The equilibrium constant for this reaction at 25°C is $7.2 \times 10^9\ M^2$(22). Light catalyzes the decomposition of hypobromous acid to hydrogen bromide and oxygen.

$$HOBr \xrightarrow{h\nu} HBr + \tfrac{1}{2}O_2$$

In the dark, hypobromous acid decomposes to bromic acid and bromine. Bromic acid is relatively unstable and decomposes slowly to give bromine and oxygen.

$$5\ HOBr \longrightarrow HBrO_3 + 2\ Br_2 + 2\ H_2O$$

$$4\ HBrO_3 \longrightarrow 2\ Br_2 + 5\ O_2 + 2\ H_2O$$

In alkaline solution, bromine reacts rapidly to produce hypobromite.

$$Br_2 + 2\,OH^- \rightleftarrows Br^- + BrO^- + H_2O \qquad K = 2 \times 10^8$$

It is necessary to maintain this reaction below 0°C to minimize the disproportionation of hypobromite to bromate and bromide.

$$3\,BrO^- \longrightarrow 2\,Br^- + BrO_3^-$$

Because they are unstable, hypobromites are usually prepared just before use for such uses as textile bleaching and desizing. In alkaline solutions at 50–80°C bromine reacts to form bromide and bromate. This reaction is reversed in acidic solutions.

$$3\,Br_2 + 6\,OH^- \longrightarrow 5\,Br^- + BrO_3^- + 3\,H_2O$$

$$5\,Br^- + BrO_3^- + 6\,H^+ \longrightarrow 3\,Br_2 + 3\,H_2O$$

3.5. Reactions with Organic Compounds.

The addition of bromine to unsaturated carbon compounds occurs readily.

$$CH_2{=}CH_2 + Br_2 \longrightarrow BrCH_2CH_2Br$$

Conjugated double bond systems usually undergo 1,4-addition.

$$CH_2{=}CH{-}CH{=}CH_2 + Br_2 \longrightarrow BrCH_2CH{=}CHCH_2Br$$

Bromine reacts directly with alkanes but this reaction has little value because mixtures are obtained. However, photochemical bromination of alkyl bromides can be quite selective (23). The bromination of aromatic hydrocarbons can occur either in a side chain or on the ring, depending on conditions. In the presence of sunlight, alkylbenzenes are brominated predominately in the side chain (24).

$$Br_2 \xrightarrow{h\nu} 2\,Br\cdot$$

$$Br\cdot + C_6H_5CH_3 \longrightarrow C_6H_5CH_2\cdot + HBr$$

$$C_6H_5CH_2\cdot + Br_2 \longrightarrow C_6H_5CH_2Br + Br\cdot$$

$$2\,Br\cdot \longrightarrow Br_2$$

In the presence of halogen Lewis acids, such as metal halides or iodine, aromatic hydrocarbons are halogenated on the ring (24). Some polynuclear aromatics, such as anthracene, can be brominated without a catalyst (23).

Phenols and phenol ethers readily undergo mono-, di-, or tribromination in inert solvents depending on the amount of bromine used. In water the main product is the 2,4,6-tribromophenol $C_6H_3Br_3O$, [118-79-6] (23). In water or acetic acid anilines also give the tribrominated product (25). Tribromophenol can be further brominated in buffered acetic acid to give 2,4,4,6-tetrabromo-2,5-cyclohexadien-1-one [20244-61-5], a useful brominating agent (26). Heterocyclic compounds range from those, such as furan, which is readily halogenated and tends to give polyhalogenated products, to pyridine, which forms a complex with aluminum chloride that can only be brominated to 50% reaction (23).

Aliphaticketones (qv) are readily brominated in the α position. Mixtures are usually obtained (24).

$$RCH_2COCH_2R + Br_2 \longrightarrow RCHBrCOCH_2R + HBr$$

Bromination of aldehydes (qv) is more complicated because bromination can take place on the aldehyde carbon as well as the α-carbon. Acetals are brominated satisfactorily in cold chloroform solution in the presence of calcium carbonate, which reacts with the hydrogen bromide formed (24).

$$2\ RCH_2CH(OC_2H_5)_2 + 2\ Br_2 + CaCO_3 \longrightarrow$$

$$2\ RCHBrCH(OC_2H_5)_2 + CaBr_2 + H_2O + CO_2\uparrow$$

Acids and esters (see Esters, organic) are less easily brominated than aldehydes or ketones. Acid chlorides and anhydrides are more easily brominated (23).

$$RCH_2COCl + Br_2 \longrightarrow RCHBrCOCl + HBr$$

Bromination of α-chloro ethers proceeds readily and often gives 90–95% yields (24).

$$RCH_2CHClOR' + Br_2 \longrightarrow RCHBrCHBrOR' + HCl$$

Bromine can replace sulfonic acid groups on aromatic rings that also contain activating groups. Phenolic sulfonic acids, for example, are polybrominated (24).

$$4{-}HOC_6H_4SO_3K + Br_2,\ H_2O \longrightarrow 2{,}4{,}6{-}Br_3C_6H_2OH + KHSO_3$$

Organometallic compounds can react with bromine to give bromides, but because organometallic compounds are frequently made from bromides the reaction with iodine to give iodides is of more synthetic significance (24).

$$RHgX + Br_2 \longrightarrow RBr + HgXBr$$

Bromine reacts with the silver salts of carboxylic acids to give an alkyl bromide containing one less carbon atom than the acid (24).

$$RCOOAg + Br_2 \longrightarrow RBr + CO_2 + AgBr$$

Amides and imides can be *N*-brominated in the cold by alkali hypobromites (24).

$$RCONH_2 + Br_2 + KOH \longrightarrow RCONHBr + KBr + H_2O$$

During some brominations a hydroxyl group can be converted to a ketone on an adjacent carbon atom (27).

$$(CH_3)_2C(OH)CH_2CH_3 + Br_2 \longrightarrow (CH_3)_2CBrCHBrCH_3 + H_2O$$

$$(CH_3)_2CBrCHBrCH_3 + H_2O \longrightarrow (CH_3)_2CHCOCH_3 + 2\ HBr$$

In the presence of base, bromine reacts with acetylenes to displace a hydrogen (28).

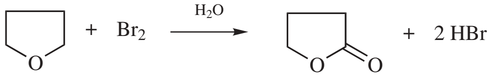
$$C_6H_5C{\equiv}CH + Br_2 + NaOH \longrightarrow C_6H_5C{\equiv}CBr + NaBr + H_2O$$

Hydrazines can be oxidized by bromine (29). Bromine has been used to synthesize organoselenium compounds (30).

In an aqueous acetate buffer at pH 5 bromine oxidizes ethers containing an α-hydrogen (31).

$$(CH_3CH_2CH_2)_2O + Br_2 \xrightarrow{H_2O} \underset{\text{Ca 100\%}}{2\ CH_3CH_2COOH} + 2\ HBr$$

$$(C_6H_5CH_2)_2O + Br_2 \xrightarrow{H_2O} \underset{\text{98\%}}{2\ C_6H_5CHO} + 2\ HBr$$



ca 100%

In the presence of a silver salt, bromine reacts with a tertiary alcohol to give a product corresponding to an insertion of oxygen (32). Bromine can oxidize certain tertiary amines to lactams (33). When tertiary alcohols are oxidized with bromine and a silver salt, tetrahydrofuran derivatives result (34).

Bromine has been used to form cyclobutane-1,2-dione [33689-28-0], $C_4H_4O_2$, when other methods failed (35,36). Regioselective bromination of ketones at the more highly substituted α-position is effected by photocatalytic bromination in the presence of 1,2-epoxycyclohexane (37).

$$CH_3COCH(CH_3)_2 + Br_2 \xrightarrow[\text{1,2-epoxycyclohexane}]{h\nu} CH_3COCBr(CH_3)_2 + HBr$$

Bromine or chlorine dissolved in hexamethylphosphoric triamide (HMPT) [680-31-9], with a base, eg, NaH_2PO_4, present, oxidizes primary and secondary alcohols to carbonyl compounds in high yield (38). Brominating epoxides in CCl_4 under irradiation gives α-bromo ketones (39).

Bromine in a two-phase system, $H_2O{-}CH_2Cl_2$, with $KHCO_3$ can convert sulfides to sulfoxides in good yields (40). Aldehydes can be directly converted to esters using bromine in alcohol solvents with sodium bicarbonate buffer (41).

Organic compounds that are easily oxidized are destroyed by bromine.

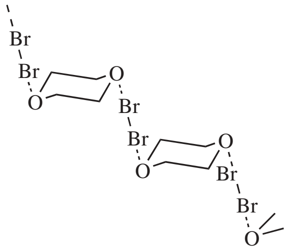
$$HCHO + 2\,Br_2 + 4\,NaOH \longrightarrow 4\,NaBr + CO_2\uparrow + 3\,H_2O$$

$$HCOOH + Br_2 \xrightarrow{H_2O} CO_2\uparrow + 2\,HBr$$

$$NH_2CONH_2 + 3\,Br_2 + 6\,NaOH \longrightarrow 6\,NaBr + N_2\uparrow + CO_2\uparrow + 5\,H_2O$$

3.6. Charge-Transfer Compounds. Similar to iodine and chlorine, bromine can form charge-transfer complexes with organic molecules that can serve as Lewis bases. The frequency of the intense ultraviolet (uv) charge transfer absorption band is dependent on the ionization potential of the donor solvent molecule. Electronic charge can be transferred from a π-electron system as in the case of aromatic compounds or from lone pairs of electrons as in ethers and amines.

Charge-transfer compounds can be isolated in the crystalline state, although low temperatures are often required. The bromine–dioxane compound, eg, has a chain structure (42).



4. Occurrence

Bromine is widely distributed in nature but in relatively small amounts. Its abundance in igneous rock is 0.00016% by weight and in seawater is 0.0065% by weight. The only natural minerals that contain bromine are some silver halides, including bromyrite AgBr, [14358-95-3], embolite Ag (Cl, Br), [1301-83-3], and iodobromite, Ag (Cl, Br, I). The biggest source of commercial bromine are the Dead Sea brines. They contain 5 g/L bromine in the open sea, 6.5 g/L in the southern basin, near Ein Bokek, and up to 12 g/L in the end brine of potash production, that is the raw material for production of bromine in Israel. Their quantity is practically unlimited. Other important sources are underground brines in Arkansas, which contain 3–5 g/L bromine, and in China, Russia, and the United Kingdom; bitterns from mined potash in France and Germany; seawater or seawater bitterns in France, India, Italy, Japan, and Spain (43).

An average of ~7 ppm of bromine is found in terrestrial plants, and edible foods contain up to 20 ppm. Among animals the highest bromide contents are found in sea life, such as fish, sponges, and crustaceans (44). Animal tissues contain 1–9 ppm of bromide and blood 5–15 ppm. The World Health Organization has set a maximum acceptable bromide intake for humans at 1 mg/kg of body weight per day. In adult males, the bromine content in serum has been found to be 3.2–5.6 μg/mL, in urine 0.3–7.0 μg/mL, and in hair 1.1–49.0 μg/mL. Bromine may be an essential trace element as are the other halides (45).

Bromine compounds are found in the atmosphere in small amounts; the sea is a primary source. Rainfall over the Pacific and Indian Oceans has been found to contain 60–80 μg/L of bromine (46). Approximately 15–20 parts per trillion (ppt) (v/v) of bromine is found in the stratosphere (47). It is up from 10 ppt a decade ago (48), maybe due to the use of brominated fire suppressants (CF_3Br, etc). The inorganic forms of Br in the stratosphere are likely involved in ozone destruction processes.

5. Manufacture

5.1. From Natural Sources.

Bromine occurs in the form of bromide in seawater and in natural brine deposits (see CHEMICALS FROM BRINE), always together with chloride. In all current methods of bromine production, chlorine, which has a higher reduction potential than bromine, is used to oxidize bromide to bromine.

$$\frac{1}{2}\,Cl_2(g) + e^- \longrightarrow Cl^- \qquad E^\circ = +1.356\ V$$

$$\frac{1}{2}\,Br_2(g) + e^- \longrightarrow Br^- \qquad E^\circ = +1.065\ V$$

$$2\,Br^- + Cl_2 \longrightarrow Br_2 + 2\,Cl^-$$

There are four principal steps in bromine production: (*1*) oxidation of bromide to bromine; (*2*) stripping bromine from the aqueous solution; (*3*) separation of bromine from the vapor; and (*4*) purification of the bromine. Most of the differences between the various bromine manufacturing processes are in the stripping and purification step.

5.2. Traditional Processes.

The two primary stripping vapors are steam and air. Steam is used when the concentration of bromine in brine is >1000 ppm. The advantage is that bromine can be condensed directly from the steam. Air is used, when seawater is the source of bromine because very large volumes of stripping gas are needed and steam would be too expensive. When air is used the bromine needs to be trapped in an alkaline or reducing solution to concentrate it.

Typical brines received at an Arkansas bromine plant have 3–5 g/L bromide, 200–250 g/L chloride, 0.15–0.20 g/L ammonia, 0.1–0.3 g/L hydrogen sulfide, 0.01–0.02 g/L iodide, and additionally may contain some dissolved organics, including natural gas and crude oil. The bromide-containing brine is first treated to remove natural gas, crude oil, and hydrogen sulfide prior to introduction into the contact tower (48).

The average composition of the liquors left from potash production in the Dead Sea, which are the raw material for production of bromine in Israel (49), was in 2001: 45 g/L calcium; 85 g/L magnesium; 350 g/L chloride; and 12 g/L bromide; L.

The biggest single bromine plant was erected by the Dead Sea in Israel, and is operated by the Dead Sea Bromine Group (DSBG). In 2000, it produced 210,000 metric tons (49).

In the steaming-out process, excess chlorine is used and recycled. The major process conditions that are measured and controlled are temperature, pressure, pH, and oxidation potential.

Materials that come in contact with wet halogens must be corrosion-resistant. Glass, ceramics, tantalum, and fluoropolymers are suitable materials. Granite has been used in steaming-out towers.

In the blowing-out process, used when the source of bromine is seawater, air is used instead of steam to strip bromine from solution. At the pH of seawater, the liberated bromine hydrolyzes to hypobromous acid and bromide. Bromide traps bromine as the tribromide ion and little bromine is released. Before stripping, enough sulfuric acid is added to the seawater to reduce the pH to 3–3.5.

The exiting air containing bromine is absorbed in a sodium carbonate solution.

$$3\ Na_2CO_3 + 3\ Br_2 \longrightarrow 5\ NaBr + NaBrO_3 + 3\ CO_2\uparrow$$

When the alkalinity of the absorbing solution becomes low it is moved to storage. Acidifying the absorbing solution with sulfuric acid reconstitutes the bromine that can then be steamed out.

$$NaBrO_3 + 5\ NaBr + 3\ H_2SO_4 \longrightarrow 3\ Br_2 + 3\ Na_2SO_4 + 3\ H_2O$$

An alternative absorbing solution uses sulfur dioxide.

$$Br_2 + SO_2 + 2\ H_2O \longrightarrow 2\ HBr + H_2SO_4$$

The bromine is recovered by oxidizing the bromide with chlorine and steaming it out of solution.

Treatment with sulfuric acid and fractional distillation are the main methods used to purify bromine. It is especially important to reduce the water content to <30 ppm to prevent corrosion of metal transportation and storage containers.

5.3. Newer Process Modifications. Patents describe a single-stage vacuum process (50) and a double-stage vacuum process (48) for recovering bromine from brines. The former is essentially the steaming-out process carried out at subatmospheric pressure. In the double-stage process the tail brines from the first stripping are stripped again under greater vacuum.

According to the patents, Arkansas brines reach the bromine plant at elevated temperatures and in the usual steaming-out process are further heated by steam to the boiling point. Additional steam is required to strip the bromine from the brine. Vacuum is used in the modified process, which, by matching the vapor pressure of the brine eliminates the need for steam to heat the brine. Because of the lower volume of steam used in the vacuum process, the capacity of a given size of contact tower is increased. A further benefit is that at the lower operating temperature of the vacuum process, chlorine undergoes fewer side reactions and

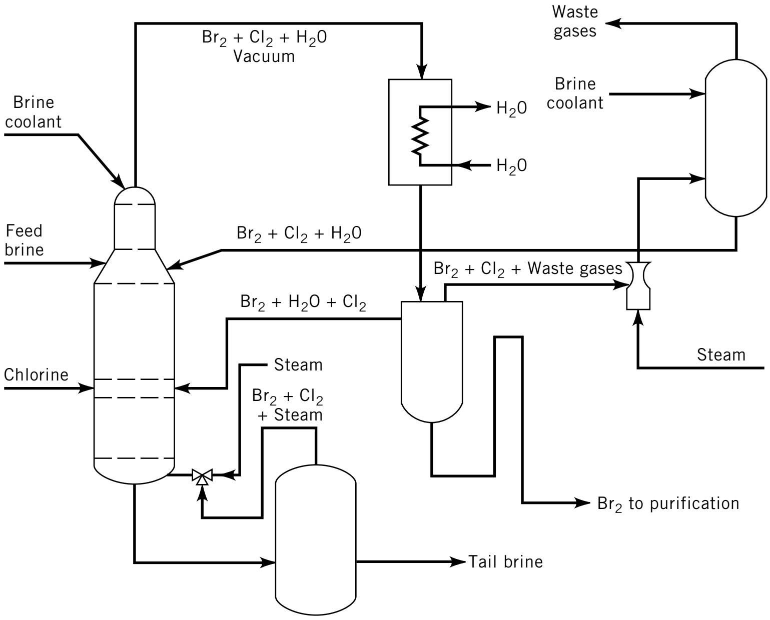


Fig. 2. Schematic of a two-stage vacuum bromine steaming-out process.

less hydrolysis so chlorine use can be reduced. In the two-stage process (Fig. 2), a second steam stripping of the tail brine is done. Other claimed advantages of the vacuum process are a reduction in the amount of lime required to treat the spent brine, lower plant maintenance costs, and decreased waste gases.

DSBG preferred to optimize its atmospheric plant rather than using vacuum. An elaborate network of heat exchangers decreased the steam consumption to 2 ton per ton bromine. DSBG claims that it is more economical than using vacuum.

A potential modification would be to replace the stripping with steam by direct extraction of the Br, resulting from the oxidation. In a process recommended in (51), after oxidation of the brines with chlorine gas, the Br_2 is extracted with CCl_4. The resulting bromine CCl_4 solution can be used for organic brominating reactions without further purification. Another method, recommended in (52) uses bromobenzene or bromotoluene to extract the bromides from natural brines containing $\sim$0.7 g bromides/L and 160 g chlorides/L. The Br^- containing extract can be used for the preparation of elemental Br_2 by oxidation, or utilized directly to make metal bromides, and various Br derivs. No industrial application of either method was reported.

From Wastes. Increasing amount of bromine is manufactured from wastes. The main source is HBr, which is obtained as a by-product in many organic reactions (see BROMINATED INORGANIC COMPOUNDS). Part of the HBr comes from incineration of organic wastes in a BRU–bromine recovery unit (see section Spills and Disposal Procedures below). The flue gases from BRU contain both HBr and Br_2, which are usually separated prior to the processing of the HBr. The basic process is similar to the production of Br_2 from bromides, ie, by oxidation with Cl_2 or other oxidating agent.

Recent researches try to recover bromine from waste hydrogen bromide streams using electrolytic membranes (53) to electrolytically decompose hydrogen bromide into its molecular constituents. These processes are not utilized yet.

Bromine Carriers. The concept of bromine carriers was developed to decrease the hazard of transportation and storage of bromine. The basic idea is to make a salt with a high concentration of bromine from the bromine and to ship it—either as a concentrated solution or as a solid—to the customers. The customer erects in his site a small bromine generator, using the standard method based on chlorine (see above). This may be useful especially for customers who have their own chlorine or at least are located near to a chlorine manufacturer, and who on the other hand are far from a source of bromine and from a port where bromine is available. Another option is to use anionic exchangers to absorb the bromine (54).

The natural choice is $CaBr_2$, which contains 80% weigh bromine, and whose 52% solution is used worldwide as a drilling fluid (see DRILLING FLUIDS). Another option may be $MgBr_2$, which contains 85% bromine.

The drawback in the use of bromine carriers is the extra cost of making the fluid from bromine, the need to prepare the bromine in-situ, and to ship chlorine (unless the customer has his own), which creates greater hazard than the bromine itself. Until now no commercial use of bromine carriers was reported.

6. Economic Aspects

Facilities for manufacturing bromine are primarily located near sources of natural brines or bitterns containing usable levels of bromine. In 1990, the United States had seven bromine plants owned by four companies. Six of the plants are in southern Arkansas and are operated by two U.S. producers: Great Lakes Chemical Corporation and Ethyl Corporation. The biggest single bromine plant is erected by the Dead Sea in Israel, and is operated by the DSBG.

The costs of building and maintaining a bromine plant are high because of the corrosiveness of brine solutions that contain chlorine and bromine and require special materials of construction. The principal operating expenses are for pumping, steam, environmental costs, energy, and chlorine. The plants are very capital intensive.

Figure 3 shows the prices of bromine (excluding shipment) in tank car quantities from 1985 to 1997 (55). The price rose 125% over these years, an aver-

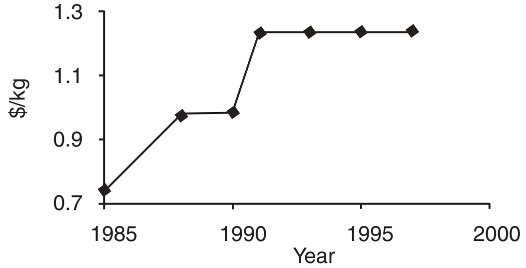


Fig. 3. Price of bromine in the period of 1985–2000.

Table 3. **Annual Bromine Production in Thousands of Metric Tons**[a]

Country	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000
Azerbaijan		5	4	3	2	2	2	2	2	2
China	12.1	16.65	24.6	31.4	32.7	41.4	50.1	40	45	45
France	3	3.2	2.29	2.19	2.26	2.024	1.974	1.95	2	2
India	1.3	1.3	1.4	1.4	1.5	1.5	1.5	1.5	1.5	1.5
Israel	135	135	135	135	130	160	180	185	185	210
Italy	0.4	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Japan	15	15	15	15	15	15	20	20	20	20
Spain	0.3	0.25	0.2	0.2	0.2	0.1	0.1	0.1	0.1	0.1
Turkmenistan	0	12	0.1	0.1	0.1	0.102	0.13	0.15	0.1	0.2
Ukraine	24[a]	7	5	3	3.5	3	3	3	3	3
United Kingdom	29.3	29.9	27.4	33.8	26.2	30.6	35.6	30	28	30
United States	170	171	177	195	218	227	247	230	239	229
Total	*390.4*	*396.6*	*392.3*	*420.4*	*431.8*	*483.0*	*541.7*	*514*	*526.0*	*543.1*

[a] Ref. 55.

Source: 1991–1993—Bromine, U.S. Bureau of Mines 1997; 1994–1999—Bromine, U.S. Bureau of Mines 1999; 2000 Bromine, U.S. Bureau of Mines 2001.

age of 7.0% a year. But the average in this case is misleading: between 1990 and 1991 the prices jumped by 25%, and remained stable since then. Even when inflation is taken into account, the price in constant dollars rose significantly. It should be mentioned that in the period of 1976–1985 the price in constant dollars fell slightly (55). The cost of shipment in bromine is high—about 60% of the price of Br, ie, ~30% of the final price of the Br is shipment costs.

Estimates of bromine production around the world are shown in Table 3.

Figure 4 shows the United States and Israel bromine production with respect to bromine production in the rest of the world. In particular, Israel, has increased its production in recent years (55,56). Between the years 1976 and 1990 U.S. production fell from 234,000 to 177,000 metric tons but it has now recovered. In the year 2000 it was back at 229,000 metric tons. Israel's production increased from 23,000 in 1976 to 210,000 metric tons at 2000.

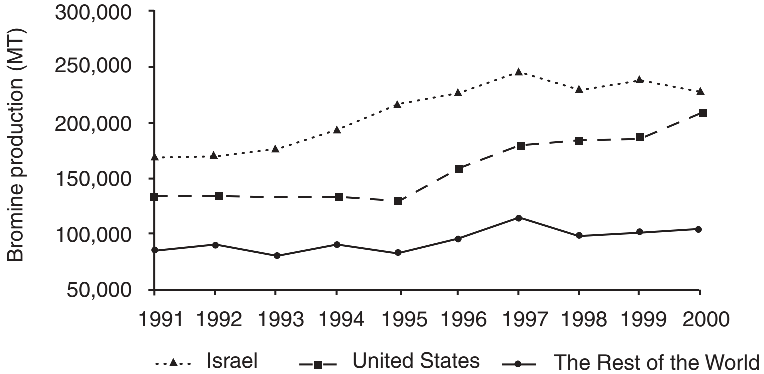


Fig. 4. Annual bromine production by the main manufacturers.

Table 4. **Bromine Specification**

Parameter	ACS requirements	Product specifications
bromine content, wt %[a]	99.5	99.9
specific gravity, 20/15°C[a]		3.1
water, ppm[b]		30
chlorine, ppm[b]	500	100
organic halogen compounds, ppm[a]	[c]	80
nonvolatile matter, ppm[a]	50	30
iodine	10	[c]
sulfur (as S)	10	[c]
heavy metals (as Pb)	2	[c]
nickel	5	[c]

[a] Minimum value.

[b] Maximum value.

[c] Must pass ACS test.

7. Requirements and Specifications

The American Chemical Society (ACS) requirements for bromine used as a reagent chemical (57) are listed in Table 4. Typical specifications for bromine produced in a modern plant (58) generally exceed these requirements.

8. Analytical Methods

To assay liquid bromine, an ampule of bromine is crushed under the surface of an aqueous potassium iodide solution and the resultant iodine ir titrated with standard sodium thiosulfate.

$$2\,I^- + Br_2 \longrightarrow I_2 + 2\,Br^-$$

$$I_2 + 2\,Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2\,NaI$$

Bromine vapor can be analyzed by the same procedure. The specific gravity of bromine is determined by hydrometer (54).

Bromine and bromides can be detected qualitatively by a number of methods. In higher concentrations bromine forms colored solutions in solvents such as carbon tetrachloride [56-23-5] and carbon disulfide [75-15-0]. Bromine reacts with yellow disodium fluorescein [518-47-8] to form red disodium tetrabromofluorescein (eosin) $C_{20}H_6Br_4Na_2O_5$, [548-26-5]. As little as 0.3 μg of bromide can be detected and chlorides do not interfere (59). Bromine reacts with platinum sulfate $Pt(SO_4)_2$, [7446-29-9], solution to form red to brown crystals of potassium hexabromoplatinate [16920-93-7], K_2PtBr_6 (60).

Impurities in bromine may be determined quantitatively (61). Weighing the residue after evaporation of a bromine sample yields the total nonvolatile matter. After removing the bromine, chloride ion may be determined by titration with mercuric nitrate, and iodide ion by titration with thiosulfate; water and organic compounds may be detected by infrared ir spectroscopy; sulfur may be determined turbidimetrically as barium sulfate; and heavy metals may be determined either colorimetrically after conversion to sulfides, or by turbidimetry. An individual metal may be detected by the dissolution of the residue and ICP determination.

Quantitative methods for determining bromide include: the Mohr method, using $AgNO_3$ titrant and potassium chromate indicator; the Volhard method using excess $AgNO_3$ titrated with potassium thiocyanate and ferric ammonium sulfate indicator; Fajans method with $AgNO_3$, as titrant, eosin as absorption indicator; silver nitrate titrant with the end point determined potentiometrically using a silver indicator electrode; and a gravimetric method as AgBr. Bromides can be detected in acidic solutions by titrating with mercuric nitrate using sodium nitroprusside indicator. Trace amounts of bromides can be determined quantitatively by (*1*) the van der Meulen method, which is useful in presence of large amounts of chloride, the bromide is oxidized to bromate and determined iodometrically; (*2*) by constant-current and constant-potential coulometry, used for fractions of a milligram up to several grams of bromide; (*3*) by ion chromography, which is useful for detecting bromide in the presence of other ions; (*4*) by polography, useful for microgram quantities (61); (*5*) by spectrophotometric methods useful for microgram quantities in the presence of chloride (68); and (*6*) by activation analysis with thermal neutrons which is useful for nanogram quantities.

Bromine in organic compounds can be determined chemically following oxidation of the organic compounds and reduction of the bromine to bromide. In the Shoniger method a few milligrams of sample is burned inside of a stoppered Erlenmeyer flask filled with oxygen. After ignition by electrical or other means, the combustion products are absorbed and the bromine content is determined acidimetrically (62,63). An alternative method employs a fusion with sodium peroxide in a Paar bomb. Infrared spectroscopy allows the determination of bromine with an accuracy of $\sim 1\%$. Neutron activation, X-ray fluorescence, ir spectroscopy, and atomic emission spectroscopy are also used to determine bromine in organic materials.

Bromine is used as an analytical reagent to determine the amount of unsaturation in organic compounds because carbon–carbon double bonds add bromine quantitatively, and for phenols that add bromine in the ortho and para positions. Standard bromine is added in excess and the amount unreacted is determined by an indirect iodine titration. Bromine is also used to oxidize several elements, such as Tl(I) to Tl(III). Excess bromine is removed by adding phenol. Bromine plus an acid, such as nitric and/or hydrochloric, provides an oxidizing acid mixture useful in dissolving metal or mineral samples prior to analysis for sulfur. Solutions of bromine in Br^- under acidic or even mildly basic conditions are used for leaching of gold and platinum group elements from ores as a quick analytical method.

9. Health and Safety Aspects and Handling

9.1. Consequences of Exposure.

Bromine has a sharp, penetrating odor. The Occupational Safety and Health Administration (OSHA) threshold limit value–time-weighted average for an 8-h workday and 40-h workweek is 0.1 ppm in air (64). Monitors are available for determining bromine concentrations in air. Concentrations of ~1 ppm are unpleasant and cause eyes to water; 10 ppm are intolerable. Inhalation of 10 ppm and higher concentrations of bromine causes severe burns to the respiratory tract and is highly toxic. Symptoms of overexposure include coughing, nose bleed, feeling of oppression, dizziness, headache, and possibly delayed abdominal pain and diarrhea. Pneumonia may be a late complication of severe exposure.

Liquid bromine produces a mild cooling sensation on first contact with the skin, which is followed by a sensation of heat. If bromine is not removed immediately by flooding with water, the skin becomes red and finally brown, resulting in a deep burn that heals slowly. Contact with concentrated vapor can also cause burns and blisters. For very small areas of contact in the laboratory, a 10% solution of sodium thiosulfate in water can neutralize bromine and such a solution should be available when working with bromine. Bromine is especially hazardous to the tissues of the eyes where severely painful and destructive burns may result from contact with either liquid or concentrated vapor. Ingestion causes severe burns to the gastrointestinal tract (65,66).

9.2. Detection of Bromine Vapor. Bromine vapor in air can be monitored by using an oxidant monitor instrument that sounds an alarm when a certain level is reached. An oxidant monitor operates on an amperometric principle. The bromine oxidizes potassium iodide in solution, producing an electrical output by depolarizing one sensor electrode. Detector tubes, useful for determining the level of respiratory protection required, contain *o*-toluidine which produces a yellow-orange stain when reacted with bromine. These tubes and sample pumps are available through safety supply companies (57). The useful concentration range is 0.2–30 ppm.

9.3. Protective Equipment. Totally enclosed systems should be used for processes involving bromine. For handling bromine in the laboratory, the minimum safety equipment should include chemical goggles, rubber gloves (Buna-*N* or neoprene rubber), laboratory coat, and fume hood. For handling bromine in a plant, safety equipment should include hard hat, goggles, neoprene full coverage slicker, Buna-*N* or neoprene rubber gloves, and neoprene boots. For escaping from an area where a bromine release has occurred, a full face respirator with an organic vapor–acid gas canister is desirable. For emergency work in an area with bromine concentrations >0.1 ppm, a self-contained breathing apparatus can be used until the air supply gets low. For longer term work in elevated bromine concentrations, an air-line respirator is essential.

9.4. Reactivity. Bromine is nonflammable but may ignite combustibles, such as dry grass, on contact. Handling bromine in a wet atmosphere, extreme heat, and temperatures low enough to cause bromine to solidify (−6°C) should be avoided. Bromine should be stored in a cool, dry area away from heat. Materials that should not be permitted to contact bromine include combustibles, liquid ammonia, aluminum, titanium, mercury, sodium, potassium, and magnesium. Bromine attacks some forms of plastics, rubber, and coatings (66).

9.5. Spills and Disposal Procedures. If a spill occurs outdoors, personnel should stay upwind of it. If the spill is in a diked area it may be possible to recover much of the bromine, by collecting it into sealable containers.

Otherwise it should be absorbed with appropriate material. Bromine vapors may be neutralized by gaseous ammonia. Small spills may be neutralized with lime water slurry (most common procedure) or 10–30% of K_2CO_3 or Na_2CO_3 solution. No decontaminants other than water should be used on humans. Under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) regulations in effect at the end of 1986, bromine is regulated as a hazardous waste or material. Therefore, it must be disposed of in an approved hazardous waste facility in compliance with the Environmental Protection Agency (EPA) and/or other applicable local, state, and federal regulations and should be handled in a manner acceptable to good waste management practice (66).

The modern procedures of disposal are based on BRU, in which the organic (sometimes mixed with inorganic) wastes are incinerated at high temperature. In one process (67), an organic bromide, eg, ethylene dibromide, is reacted in the gas phase with H_2 at 400–500°C in the presence of a catalyst to prepare HBr. Pelleted Al_2O_3-supported Cr_2O_3 cracking catalyst is suitable. The Br recovery as HBr is ~95%. The process makes it possible to ship organic bromides as sources of HBr. Recent processes operate at very high temperatures (>1000°C), to prevent the creation and survival of brominated dioxins, and the resulting bromine and hydrogen bromide are recovered by absorption in water and release by distillation. The hydrogen bromide may be further oxidized to yield bromine (see section on Bromine Manufacturing from Wastes). The costs of the incineration exceed the commercial value of the recoved bromine values, but as it is the only effective way to get rid of brominated organic wastes, without creating an ecological hazard, they become an integral part of more and more bromine manufacturing plants.

An example of disposal is the recovery of bromine from Br-containing photographic wastewater, which is done by spray incineration of the wastewater with alkali metal hydroxides or salts under an oxidative atmosphere, collection of the ashes formed by the incineration in water, and treatment of the aqueous salt solutions with Cl_2 to recover the bromine (68).

9.6. Materials of Construction. Glass has excellent corrosion-resistance to wet or dry bromine. Lead is very useful for bromine service if water is <70 ppm. The bromine corrosion rate increases with concentrations of water and organics. Tantalum and niobium have excellent corrosion-resistance to wet or dry bromine. Nickel and nickel alloys such as Monel 400 and Hastelloys B and C have useful resistance for dry bromine but is rapidly attacked by wet bromine. Steel and stainless steel materials are not recommended. The fluoropolymers Kynar, Halar, and Teflon are highly resistant to bromine but are somewhat permeable. The rate depends on temperature, pressure, and structure (density) of the fluoropolymer (69). Other polymers are not recommended.

9.7. Storage and Transportation. Bromine in bulk quantities is shipped in the United States in 7570 and 15,140 L lead-lined pressure tank cars or 6435–6813 L nickel-clad pressure tank trailers. The trailers must be filled at least 92% full to prevent inertia effects of the heavy liquid while on the highway. International shipments made by DSBG are in 15.2–23.3 metric ton (volume of 5300–8000 L), lead-lined tanks containers (isotanks). For smaller quantities lead lined tanks ("goslars") of 3.5 metric tons (four tanks packed on one isoframe) and cylinders of 400 kg are used. The relatively high freezing point of bromine (−7.25°C) may cause some problems in shipping and storage. If bromine has frozen in a tank car, it is necessary to circulate warm (below 54°C) water through the heating coils.

Dry nitrogen gas is recommended for use in pressure transferring bromine, although dry (−40°C dew point) air may be used. The gas used to pad the bromine in the storage tank must be absolutely dry or severe corrosion results. Dry bromine picks up water from air having a dew point of −70°C. When exposed to a high humidity atmosphere the water content of bromine can exceed 300 ppm. Bromine is nonreactive to lead, monel, and a few other alloys when water content is <30 ppm. If the water content increases above 70 ppm, corrosivity to many metals increases greatly. Fluorinated plastics are widely used in equipment, piping, valves, and gaskets.

The concept of shipping solid bromine was considered on a R&D level and verified in a pilot plant (70), but has not been commercially implemented. The basic idea is to freeze the bromine inside a cooled isotank, and keep it cooled during the ship transport. The main advantage of this method is, that in the case of an accident that results in dropping the tank into the sea, in the port or on the highway, there is enough time for a rescue operation, before thawing of the solid, decreasing the risk of liquid and vapor spillage.

10. Uses

An important use of bromine compounds is in the production of flame retardants (qv). These are of the additive-type, which is physically blended into polymers, and the reactive type, which chemically reacts during the formation of the polymer. Bromine compounds are also used in fire extinguishers. Brominated polymers are used in flame retardant applications and bromine-containing epoxy sealants are used in semiconductor devices.

Bromine has some use in swimming pools and in bleaching. It is also a disinfectant for cooling water and wastewater. Its main use is as a chemical reactant. Bromine compounds are frequently intermediates in the production of other organic chemicals. Bromine is found in certain dyes. Bromides have been used for many years in the pharmaceutical industry as sedatives and as intermediates for drugs. Some therapeutic powers are claimed for certain iodine–bromine spa waters. Alkali bromides are used in the photographic industry. Bromine is used in making some perfumes and certain bromine compounds are disinfectants, eg, bromochlorodimethylhydantoin, which is used in swimming pools and spas.

Zinc–bromine storage batteries (qv) are under development as load-leveling devices in electric utilities (71). Photovoltaic batteries have been made of selenium or boron doped with bromine. Graphite fibers and certain polymers can be made electrically conductive by being doped with bromine. Bromine is used in quartz–halide light bulbs. Bromine is used to etchaluminum, copper, and semi-conductors. Bromine and its salts are known to recover gold and other precious metals from their ores (72). Gold, as a precious metal, is found naturally as an element, at very low concentration . A mixture of bromine and bromide salts

Table 5. **Consumption of Bromine by End Users (Thousands of Metric Tons)**[a,b]

	1965	1970	1975	1980	1985	1990	1993	1996
flame retardants	5.9	7.7	21.8	25.4	48	73	79	89.8
drilling fluids	[d]	[d]	[d]	[d]	18	21.8	12.2	54
brominated agr. chemicals	4.5	7.7	9.1	15.3	17.2	23.3	29.5	28.5
biocides/water treatment	[b]	[b]	[b]	[b]	6.7	9.8	7.7	15.9
gasoline additives	81.6	111.2	98	72.6	32	14	10.9	neg.
others[c]	25	29.5	54.2	54.6	20.3	32.9	32.5	36.5
Total	*117*	*156.1*	*183.1*	*167.9*	*142.2*	*174.8*	*171.8*	*224.7*

[a] Data through 1982 are compiled annually from a voluntary survey. Data are not complete because many smaller bromine consumers are not included. In addition, data may not be reported consistently by different end users.

[b] Reference (56).

[c] Includes bromobutyl rubber, photographic chemicals, dyes, pharmaceuticals and brominated intermediates. Data for 1955–1980 also include drilling fluids, biocides, and water treatment chemicals.

[d] Included in "Others".

may serve as an oxidant and complexant of the gold, according to the overall formula:

$$2\ \mathrm{Au} + 3\ \mathrm{Br} \longrightarrow 2\ \mathrm{AuBr_4}]^- + \mathrm{Br}^-$$

The complex is reduced back to a metal, adsorbed on carbon granules, either in CIS (carbon in solution) or CIP (carbon granules) process. This bromine route is much quicker and efficient than the standard cyanide process, and significantly less toxic. In a process developed by Kaljas (73) and tested in Australia in 1989 and 1992 by Reid and Storhok (72), the CIP technique was applied successfully, at ambient temperature, at pH <10, using 0.3% bromine. No industrial application has been reported.

Bromine can be used to desulfurize fine coal (see COAL CONVERSION PROCESSES; CLEANING AND DESULFURIZATION). Table 5 shows estimates of the primary uses of bromine.

BIBLIOGRAPHY

"Bromine" in *ECT* 1st ed., Vol. 2, pp. 629–645, by V. A. Stenger, The Dow Chemical Company; in *ECT* 2nd ed., Vol. 3, pp. 750–766, by V. A. Stenger, The Dow Chemical Company; in *ECT* 3rd ed., Vol. 4, pp. 226–241, by C. E. Reineke, Dow Chemical U.S.A.; "Bromine" in *ECT* 4th ed., Vol. 4, pp. 536–560, by Philip F. Jackisch, Ethyl Corporation; "Bromine" in *ECT* (online), posting date: December 4, 2000, by Philip F. Jackisch, Ethyl Corporation.

CITED PUBLICATIONS

1. M. C. Sneed, J. L. Maynard, and R. C. Brasted, *Comprehensive Inorganic Chemistry*, Vol. **3**, D. Van Nostrand, New York, 1954, p. 70.
2. A. J. Downs and C. J. Adams, in A. F. Trotman-Dickenson, ed., *Comprehensive Inorganic Chemistry*, Pergamon Press, New York, 1973, p. 1107.

3. F. Yaron, in Z. E. Jolles, ed., *Bromine and Its Compounds*, Ernest Benn Ltd., London, 1966, 43–49.
4. V. A. Stenger, *Angew. Chem. Int. Ed.* **5**(3), 280 (1966).
5. *Bromine—Unloading, Storing, Handling*, Form No. 101-2-76, Dow Chemical U.S.A., 1976.
6. G. H. Cady, *J. Phys. Chem.* **89**, 3302 (1985).
7. J. d'Ans and P. Hofer, *Angew Chem.* **47**, 71 (1934).
8. F. H. Rhodes and C. H. Bascom, *Ind. Eng. Chem. Ind. Ed.* **19**, 480 (1927).
9. L. W. Winkler, *Chem. Ztg.* **23**, 687 (1899).
10. W. F. Linke, ed., *Solubilities Inorganic and Metal–Organic Compounds*, 4th ed., Vol. **1**, American Chemical Society, Washington, D.C., 1958, 442–444.
11. A. I. Popov, in V. Guttman, ed., *Halogen Chemistry*, Vol. **1**, Academic Press, New York, 1967, p. 225.
12. U.S. Pat. 2,481,455 (Sept. 6, 1949), W. R. Kramer and V. A. Stenger (to The Dow Chemical Company).
13. Ref. 10, p. 161.
14. U.S. Pat. 5,008,477 (Apr. 16, 1991), S. Hussain (to Ethyl Corp.).
15. J. Kleinberg, W. J. Argersinger, Jr., and E. Griswold, *Inorganic Chemistry*, D. C. Heath, Boston, Mass., 1960, Chapt. 16.
16. E. S. Gould, *Inorganic Reactions and Structure*, Henry Holt, New York, 1955, Chapt. 14.
17. Ref. 1, p. 118.
18. H. S. Booth, ed., *Inorganic Syntheses*, McGraw-Hill, New York, 1939, p. 51.
19. R. B. Heslop and P. L. Robinson, *Inorganic Chemistry*, 3rd ed., Elsevier, Amsterdam, The Netherlands, 1967, Chapt. 28.
20. T. Moeller, *Inorganic Chemistry*, John Wiley & Sons, Inc., New York, 1952, Chapt. 13.
21. R. C. Weast, ed., *CRC Handbook of Chemistry and Physics*, CRC Press, Boca Raton, Fla., 70th ed., 1989, p. D152.
22. A. J. Downs and C. J. Adams, in A. F. Trotman-Dickenson, ed., *Comprehensive Inorganic Chemistry*, Pergamon Press, New York, 1973, p. 1191.
23. C. A. Buehler and D. E. Pearson, *Survey of Organic Syntheses*, Wiley-Interscience, New York, 1970, Chapt. 7.
24. R. B. Wagner and H. D. Zook, *Synthetic Organic Chemistry*, John Wiley & Sons, Inc., New York, 1953, Chapt. 4.
25. F. Yaron, in Z. E. Jolles, ed., *Bromine and its Compounds*, Academic Press, New York, 1966, 71–72.
26. G. J. Fox, G. Hallas, J. D. Hepworth, and K. N. Paskins, *Org. Synth.* **VI**, 181 (1988).
27. F. C. Whitmore, W. L. Evers, and H. S. Rothrock, *Org. Synth.* **II**, 408 (1943).
28. S. I. Miller, G. R. Ziegler, and R. Wieleseck, *Org. Synth.* **V**, 921 (1973).
29. P. A. Wender, M. A. Eissenstat, N. Sapuppo, and F. E. Ziegler, *Org. Synth.* **VI**, 334 (1988).
30. L. Blanco, P. Amice, and J. M. Conia, *Synthesis*, 194 (1976).
31. N. C. Deno and N. H. Potter, *J. Am. Chem. Soc.* **89**, 3550 (1967).
32. R. A. Sneen and N. P. Matheny, *J. Am. Chem. Soc.* **86**, 3905 (1964).
33. A. Picot and X. Lusinchi, *Synthesis*, 109 (1975).
34. N. M. Roscher and E. J. Jedziniak, *Tetrahedron Lett.*, 1049 (1973).
35. H.-G. Heine, *Ber. Dtsch. Chem. Ges.* **104**, 2869 (1971).
36. J. M. Conia and J. M. Denis, *Tetrahedron Lett.*, 2845 (1971).
37. V. Calo, L. Lopez, and G. Pesce, *J. Chem. Soc. Perkin Trans. I*, 501 (1977).
38. M. Al Neirabeyeth, J.-C. Ziegler, and B. Gross, *Synthesis*, 811 (1976).
39. V. Calo, L. Lopez, and D. S. Valentino, *Synthesis*, 139 (1978).
40. J. Drabowicz, W. Midura, and M. Mikolajczyk, *Synthesis*, 39 (1979).

41. D. R. Williams, F. D. Klingler, E. E. Allen, and F. W. Lichtenthaler, *Tetrahedron Lett.* **29**(40), 5087 (1988).
42. F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 2nd ed., Wiley-Interscience, New York, 1966, 563–564.
43. P. A. Lyday, in *Minerals Yearbook 1987*, Vol. **1**, U.S. Bureau of Mines, Washington, D.C., p. 172.
44. P. J. Scheuer, *Chemistry of Marine Nature Products*, Academic Press, New York, 1973.
45. R. E. Cuenca, W. J. Pories, and J. Bray, *Biol. Trace Elem. Res.* **16**(2), 151 (1988).
46. G. D. Supatashvili and G. A. Makharadze, *Soobshch. Adad. Nauk Gruz. SSR* **120**(1), 121 (1985).
47. S. C. Wofsy, M. B. McElroy, and Y. L. Yung, *Proc. Conf. Clim. Impact Assess. Program, 4th 1975*, 286 (1976).
48. U.S. Pat. 4,719,096 (Jan. 12, 1988), K. C. Lesher and H. W. Henry (to Ethyl Corp.).
49.
DSBG Internal Data
50. U.S. Pat. 4,725,425 (Feb. 16, 1988), K. C. Lesher and H. W. Henry (to Ethyl Corp.).
51. A. P. Krasnov, V. F. Trifonov, O. V. Lebedev, *Khim. Prom-st.* (Moscow) (1986), (**4**), 221
52. C. Yang, Z. Wang, H. Xiao, L. D. X. Nanjing, **23**(5), 466 (1999) (in Chinese)
53. C. N. Wauters, J. Winnick, *AIChE* **44** p. 2144 (10 Oct 1998)
54. Rus. Pat. 2070537 (Dec. 20, 1996) Y. N. Fedulov, L. L. Koroleva, L. N. Pisarenko, N. P. Sokolova, V. Danilov,
55. *Bromine*, U.S. Bureau of Mines, Washington, D.C., annual issues from 1975 to 2001.
56. CEH, 1998 by the Chemicals Economics Handbook - SRI International.
57. *Reagent Chemicals*, 7th ed., American Chemical Society, Washington, D.C., 1986, 158–160.
58. *Bromine*, Ethyl Corp., Baton Rouge, La., Jan. 1985, p. 7.
59. N. D. Cheronis and J. B. Entrikin, *Semimicro Qualitative Organic Analysis*, Wiley-Interscience, New York, 1957, p. 179.
60. G. W. Armstrong, H. H. Gill, and R. F. Rolf, “The Halogens,” in *Treatise on Analytical Chemistry*, Part II, Vol. **7**, Wiley-Interscience, New York, 1961.
61. F. Feigl and V. Anger, *Spot Tests in Inorganic Analysis*, Vol. **1**, Elsevier, New York, 1972, p. 143.
62. W. Shoniger, *Mikrochim. Acta*, 123 (1955).
63. *Ibid.*, 869 (1956).
64. *Threshold Limit Values and Biological Exposure Indices for 1989–1990*, American Conference of Governmental Industrial Hygienists, Cincinnati, Ohio, 1989, p. 14.
65. *Material Safety Data Sheet: Bromine*, Ethyl Corp., Baton Rouge, La., Sept. 20, 1991.
66. *Bromine Safe Handling Seminar*, Ethyl Corp., Magnolia, Ark., Oct. 4–6, 1988.
67. U.S. Pat. 3919398 (Nov. 11, 1975), R. A. Davis, (for Dow Chemical Co., USA).
68. Jap. Pat. 07171581 (July 11, 1995), M. Yamada and T. Nakamura, H. Asano, and T. Adachi (for Fuji Photo Film Co. Ltd, Japan).
69. “Chemical Profile: Bromine” in *Chem. Mark. Rep.* (Apr. 16, 1979); (Apr. 22, 1982); (July 22, 1985); (July 11, 1988); and (July 15, 1991).
70. S. Wajc, IMI(TAMI) Internal Report (1997)
71. T. N. Veziroglu, ed., “Alternate Energy Sources,” *Proceedings of the Miami International Conference*, Vol. **1**, Hemisphere, Washington, D.C., 1983, 327–333.
72. M. Freiberg, *Rev. Chem. Eng.*, **9**, 3–4, 333, (1993)
73. U.S. Pat. 4684404 (Aug. 4, 1987), Gui I. Z. Kalocsal (for Kaljas Ltd., Australia).

GENERAL REFERENCES

Z. E. Jolles, ed., *Bromine and its Compounds*, Academic Press, New York, 1966.

V. Gutmann, ed., *MTP Int. Rev. Sci.: Inorg. Chem., Ser. One*, **3** (1972).

A. J. Downs and C. J. Adams, “Chlorine, Bromine, Iodine, and Astatine,” in J. C. Bailar, Jr. and co-eds., *Comprehensive Inorganic Chemistry*, Vol. **2**, Pergamon Press, Oxford, 1973, 1107–1594.

V. Gutmann, ed., *Halogen Chemistry*, Academic Press, New York, 1967 (three volumes).

BARUCH GRINBAUM
IMI(TAMI) Institute for
Research and Development
MIRA FREIBERG
Dead Sea Bromine Group