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## 1. Introduction

Bromine, Br [7726-95-6], a nonmetallic element of the halogen family, is a dark red-brown liquid at ordinary temperatures and pressures. It appears in group 7 A, period 4 of the periodic table between chlorine and iodine. The name is derived from the Greek *βρωμος*, meaning stench. It vaporizes readily and has a sharp, penetrating odor. The electronic configuration is:  $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^5$ ; the most common oxidation states are  $-1$  and  $+5$ . Valences of  $+3$ ,  $+1$ , and  $+7$  are also observed.

Bromine was first discovered by A. J. BALARD in 1824. He had isolated the element while studying the flora of a salt marsh near Montpellier, France. He noticed a deposit of sodium sulfate which had crystallized in a pan containing mother liquor from common salt. Investigating uses for the waste liquors, BALARD observed that upon saturation with chlorine, the new red liquid could be obtained by distillation [1]. CARL LÖWIG [2] independently isolated bromine at Kreuznach, Germany, in 1825 and was in the process of studying its properties

when BALARD's paper appeared. Bromine had been prepared earlier by JOSS and LIEBIG but neither of them recognized that it was an element [3].

The first mineral to contain bromine was discovered in 1841 by BERTHIER; the mineral was apparently bromyrite (silver bromide).

The first commercial production of bromine was from native salt brines in 1846 at Freeport, Pennsylvania, by DAVID ALTER. The "blowing out" process for Midland, Michigan brines was invented by HERBERT DOW in 1899. The Dow process for extracting bromine from seawater began in 1934 near Wilmington, North Carolina.

Bromine does not occur in nature as the free element but is found solely as the bromide. There are only a few bromine-containing minerals, all silver ores, among which are bromyrite,  $\text{AgBr}$ ; embolite,  $\text{Ag}(\text{Cl}, \text{Br})$ ; and iodobromite,  $\text{Ag}(\text{Br}, \text{Cl}, \text{I})$ . Bromine usually follows chlorine through the geochemical cycle. Crystal rocks contain 2–3 ppm bromine. The total bromine content in the crust of the earth has been estimated to be 0.0003%.

Bromine also appears in variable amounts in the biosphere. The bromide concentration in terrestrial plants is about 7 ppm and in freshwater plants, 22 ppm. The amounts of bromide found in some edible foods are wheat flour, 19.7 ppm; potatoes, 10.3 ppm; oranges, 3 ppm; and apples, 4 ppm.

In the animal world, the highest bromide contents are found in sea life, such as fish, sponges, and crustaceans [4]. Many natural products containing organic bromine have been isolated, such as dibromo-indigo (Tyrian purple) from sea snails, bromoform from red algae, and brominated phenols and diphenyl oxides from sponges and marine bacteria [5]. Animal tissues contain between 1 and 9 ppm bromide and blood bromide ranges between 5 and 15 ppm.

The most easily recoverable bromine occurs in the hydrosphere as soluble bromide salts. The concentration of bromine in seawater is about 65 mg/L. Other sources of extractable bromine occur in salt lakes, salines, and inland seas (Table 1). The Dead Sea is one of the richest commercial sources of Br, containing nearly 5 g/L of bromide at the sea surface, 6.5 g/L in the southern basin near Ein Bokek and up to 12 g/L in the end brine of potash production,

which serves as the raw material for Israeli bromine production. The Dead Sea has been estimated to contain 1 billion/t of bromine.

The most important source of bromine is brine wells, which is the principal source in the United States. The richest brines are found in Arkansas and Michigan, with bromide content ranging from 2 to 5 g/L.

A few bromine molecules per trillion (ppt) causes the complete destruction of ozone in the lower troposphere during polar spring and about half of the losses associated with the ozone hole in the stratosphere [6]. Over the last three decades, field and aerial measurements of BrO in the free troposphere suggest an even more pervasive global role for bromine [7].

BrO has been found in the boundary layer during polar ozone depletion events [8], over salt lakes [9], in the marine boundary layer [10] and also in volcanic plumes [11].

## 2. Physical Properties

Bromine [7726-95-6],  $^{20}\text{Br}$ ,  $M_r$  159.808 (for  $\text{Br}_2$ ), stable isotopes 79 (50.54%), 81 (49.46%), is a dense, dark red, fuming, highly

**Table 1.** Bromine occurrence

	Original content, g/L	After concentration, g/L
Sea water	0.065	
Inland seas		
Kharaghoda, Indian Ocean	0.25	6
Sasyk Lake, Black Sea	0.28	1.5–4.5
Shebhka el Melah, Tunisia	2.5	6.8
Salt lakes		
Dead Sea, Israel	4–6	12–13
Elton lake Russia	0.63–2.25	
Searles Lake, Calif. (USA)	0.85	
Brine wells		
Michigan, (USA)	2–3	
Arkansas, (USA)	4–5	
Yakutsk, Siberia, Russia	6–7 (CaCl <sub>2</sub> solution)	
Mineral salt deposits	wt%	
Rock salt	0.005–0.040	
Sylvite	0.117–0.300	
Carnallite	0.155–0.334	
Bischofite	0.467	
Tachydrite	0.438	
Hard salt	0.05–0.20	

corrosive, and lacrimatory liquid. Its strong pungent odor is detectable at 1 ppm by volume in air. The color of bromine varies with temperature (yellow orange at 20 K, orange red, red brown, to almost black at its melting point). Liquid bromine is always dark red, whereas, bromine vapors are usually orange to red brown. The absorption band for liquid bromine lies between 417–420 nm [12].

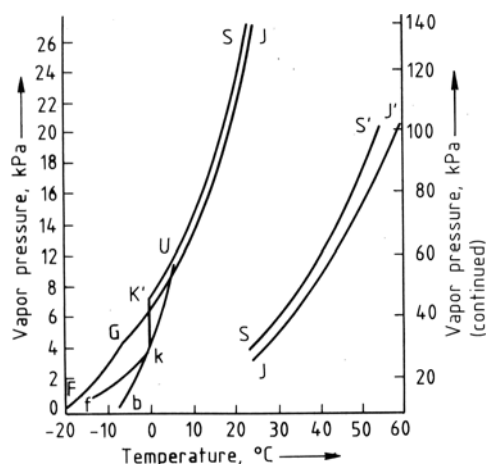
The physical properties of elemental bromine are summarized in Table 2. The vapor pressure curve is shown in Figure 1. Both bromine liquid and vapor, up to a temperature of about 600 °C, are diatomic (Br<sub>2</sub>).

The density,  $\rho$ , of liquid bromine (in g/L) in the range 0–50 °C can be calculated using the following equation ( $T$  is temperature in K):

$$\rho = 4.1295 - 0.003447 T$$

**Table 2.** Physical properties of bromine [13–16]

$f_p$ , °C	–7.25
$bp$ , °C	58.8
Density, g/cm <sup>3</sup> , 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	7.139
Refractive index, 20 °C	1.6083
25 °C	1.6475
Viscosity, mm <sup>2</sup> /s (= cSt), 20 °C	0.314
30 °C	0.288
40 °C	0.264
50 °C	0.245
Surface tension, mN/m (= dyn/cm), 25 °C	40.9
Solubility parameter, J/cm <sup>3</sup> (25 °C)	23.5
Critical temperature, °C	311
Critical pressure, MPa (atm)	10.3 (102)
Thermal conductivity, W m <sup>–1</sup> K <sup>–1</sup>	0.123
Specific conductivity, ( $\Omega \cdot \text{cm}$ ) <sup>–1</sup>	$9.10 \times 10^{-12}$
Dielectric constant, 25 °C, 10 <sup>5</sup> Hz	3.33
Electrical resistivity, 25 °C, $\Omega \cdot \text{cm}$	$6.5 \times 10^{10}$
Expansion coefficient at 20–30 °C, K <sup>–1</sup>	0.0011
Compressibility, 20 °C (0–10 MPa)	$62.5 \times 10^{-6}$
Heat of vaporization, J/g, 50 °C	187
Heat of fusion, J/g, –7.25 °C	66.11
Heat capacity, J/mol, 15 K [17]	7.217
30 K	22.443
60 K	36.33
240 K	57.94
solid, 265.9 K	61.64
liquid, 265.9 K	77.735
Electronegativity	3.0
Electron affinity, kJ	330.5



**Figure 1.** Vapor pressure curves for Br<sub>2</sub> and water saturated with Br<sub>2</sub>  
 FGJ–JJ': vapor-pressure curve of Br<sub>2</sub>; f (b)k(K')US–SS': vapor-pressure curve of Br<sub>2</sub>-containing water; f–K: Br<sub>2</sub> hydrate + ice + vapor; b–K (metastable), k–U (stable): Br<sub>2</sub> hydrate + solution + vapor; k–K' (metastable): ice + solution + vapor; K'–U (metastable), U–S, S–S' (stable): Br<sub>2</sub> + solution + vapor; for S–S', J–J' use right-hand axis

The dynamic viscosity,  $\eta$ , in Pa · s, can be determined ( $T$  is temperature in K):

$$\eta = (7.0274 \times 10^{-3} T^2 + 6.037 T - 1368)^{-1}$$

An important reaction of elemental bromine is its dissociation:



Some data for this reaction are shown in Tables 3 and 4. The free energy  $\Delta F^\circ$  (149 640 J at 298.1 K) is calculated by using the following equation:

$$\Delta F^\circ = 174170 - 10.886 T \ln T + 0.0020934 T^2 - 20934 T^{-1}$$

Bromine exhibits moderate solubility in water at 25 °C, i.e., 33.6 g/L. The aqueous solubility of bromine in the temperature range of –0.3–53.6 °C is given in Table 5.

**Table 3.** Equilibrium constants for Equation 1

$T$ , °C	650	800	900	1000
Log $K$	–5.983	–3.747	–2.854	–2.114

**Table 4.** Thermodynamic data for molecular and atomic bromine

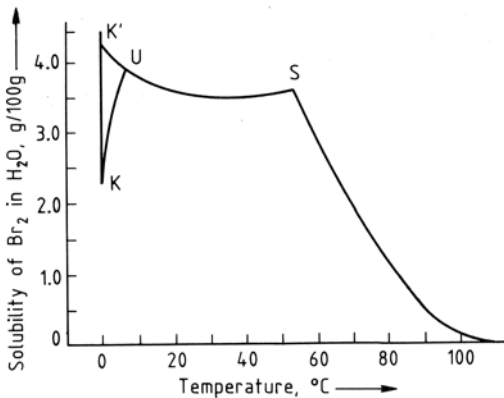
	$\Delta H^\circ$ , J	$\Delta G^\circ$ , J	$S^\circ$ , J/K
Br	111788	82480	175.0
Br <sub>2</sub> (g)	30564	2931	245.3
Br <sub>2</sub> (l)	0	0	152.4

**Table 5.** Solubility of bromine in water [18]

$T$ , °C	wt %	$T$ , °C	wt %
−0.3	2.23	30.1	3.341
0	2.28	36	3.357
3	3.08	41	3.387
5.8	3.73	44.8	3.414
10	3.60	48.8	3.447
20	3.41	52.8	3.496
25	3.39	53.6	3.50

The solubility curve for bromine in water is presented in Figure 2.

Bromine forms a red crystalline hydrate, Br<sub>2</sub> · 8 H<sub>2</sub>O, which decomposes at 5.8 °C [20]. Bromine hydrate and ice form a eutectic at −6.3 °C. Because of the slow formation of bromine hydrate, bromine in water solution is metastable and forms ice and bromine below −58 °C.



**Figure 2.** Solubility diagram for Br<sub>2</sub>—H<sub>2</sub>O at 101.3 kPa [19]

K': 4.3 g (−0.58 °C), Br<sub>2</sub>(l) + ice + H<sub>2</sub>O; K: 2.27 g (−0.3 °C), Br<sub>2</sub>(hydrate) + ice + H<sub>2</sub>O; U: 3.86 g (5.84 °C), Br<sub>2</sub>(hydrate) + Br<sub>2</sub>(l) + H<sub>2</sub>O; S: 3.58 g (54.3 °C), *bp*

**Table 6.** Solubility of bromine in various aqueous solutions at 25 °C [22, 23]

Solute	$c_{\text{solute}}$ , g/L	$c_{\text{Br}_2}$ , g/L	Solute	$c_{\text{solute}}$ , g/L	$c_{\text{Br}_2}$ , g/L
None	—	34.0	NaCl	58.5	55.9
NaBr	92.6	99.2	NaCl*	118.0	86.4
NaBr	206.0	248.0	KNO <sub>3</sub>	101.2	29.0
NaBr	320.0	546.0	NaNO <sub>3</sub>	85.1	28.0
KBr	11.9	49.3	K <sub>2</sub> SO <sub>4</sub>	91.2	24.8
KBr	59.5	119.0	Na <sub>2</sub> SO <sub>4</sub>	63.6	23.9
KBr	119.0	216.0	H <sub>2</sub> SO <sub>4</sub>	49.0	29.3
KBr	360.8	632.0	HBr*	33.7	108.8
KCl	74.6	57.4	HCl*	39.0	79.2

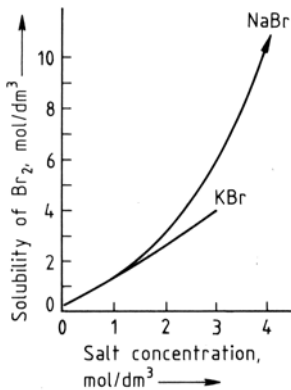
\* At 20.6 °C

The density of water containing bromine ( $\rho_T$  in g/mL) can be determined using the formula:

$$\rho_T = 1.0995 + 0.0073 w_{\text{Br}} - 0.000344T$$

where  $w_{\text{Br}}$  is the bromine concentration in % and  $T$  the temperature in K. Bromine can be recovered quantitatively from a water solution by sparging with air [21]. The solubility of bromine in water can be increased by adding bromide and chloride salts because of polyhalide complex formation (Table 6). Equilibrium constants for the formation of tribromide and pentabromide ions at 25 °C have been determined [24]:

The relationship between bromine solubility and the concentration of NaBr and KBr salts is shown in Figure 3.



**Figure 3.** Bromine solubility in salt solutions at 25 °C

Bromine and chlorine are miscible in all proportions, yielding an equilibrium mixture containing the interhalogen compound bromine chloride (BrCl);



This equilibrium mixture can be separated by distillation [17]. The density of bromine-chlorine mixtures ( $\rho_T$  in g/L) can be calculated using the following formula:

$$\rho_T = 4.0916 - 0.0374 w_{\text{Cl}} - 0.0033 T$$

where  $w_{\text{Cl}}$  is the concentration of chlorine in % and  $T$  is the temperature in K.

The solubility of water in liquid bromine is relatively low (380 ppm at  $25^\circ\text{C}$ , Fig. 4). Commercial bromine usually contains less than 30 ppm water, but bromine has an affinity for moisture and may pick up additional water if improperly handled. For instance, at room temperature, it could reach a water content of 70 ppm if contacted with air at 20% relative humidity (R.H.). This could rise to 300 ppm if the bromine is exposed to air having 80% R.H., a level that increases considerably bromine's corrosive properties [16].

Bromine is miscible with many organic solvents, such as carbon tetrachloride, ether, methanol, alkyl bromides, methylene chloride, chloroform, and acetic acid. Reactions can take place with some of these solvents under certain conditions.

Bromine itself is a good solvent for cesium bromide, as shown in Table 7 along with the solubility of other salts in liquid bromine. This provides a method for separating cesium bromide from the other alkali bromides.

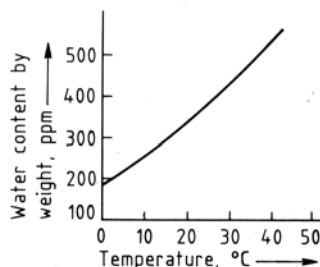


Figure 4. Solubility of water in bromine

Table 7. Solubility of various salts in liquid bromine, g/100 g solution [15]

LiBr	0.005	SrBr <sub>2</sub>	0.002
NaBr	0.010	BaBr <sub>2</sub>	0.005
KBr	0.0185	NiBr <sub>2</sub>	0.0003
RbBr	0.058	ZnBr <sub>2</sub>	0.0146
CsBr	19.3	FeBr <sub>3</sub>	0.324
MgBr <sub>2</sub>	0.002	AlBr <sub>3</sub>	0.002
CaBr <sub>2</sub>	0.003		

### 3. Chemical Properties

Many chemical reactions of bromine are a result of its strong oxidizing properties. The tendency of bromine to gain a single electron lies as expected between chlorine and iodine, as do most other chemical properties. Bromine is only a moderately strong oxidizing agent (Table 8).

Corresponding to its position in the electro-motive series, chlorine oxidizes bromide ion to elemental bromine. This reaction is the chemical basis for the production of bromine (see Chap. 4).

Of the bromine fluoride compounds (BrF, BrF<sub>3</sub>, BrF<sub>5</sub>), BrF<sub>3</sub> is of greatest practical importance because of its use in fluorinating organic substances. Bromine trifluoride reacts explosively with water and hydrocarbon tap greases, and reacts vigorously with B, C, Si, As, Sb, I, and S to form fluorides [25].

Bromine undergoes *reduction* to bromide in water. The reducing agent can be either the water itself or the remaining bromine. In the former case, oxygen is formed:

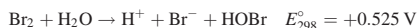


Table 8. Standard potentials of bromine and various other oxidizing agents

I <sub>2</sub> (s) / 2 I <sup>-</sup>	+ 0.53 V
Br <sub>2</sub> (l) / 2 Br <sup>-</sup>	+ 1.07 V
Cl <sub>2</sub> (g) / 2 Cl <sup>-</sup>	+ 1.36 V
F <sub>2</sub> (g) / 2 F <sup>-</sup>	+ 2.85 V
Fe <sup>3+</sup> / Fe <sup>2+</sup>	+ 0.77 V
Ce <sup>4+</sup> / Ce <sup>3+</sup>	+ 1.44 V
MnO <sub>4</sub> / Mn <sup>2+</sup>	+ 1.52 V
Pb <sup>4+</sup> / Pb <sup>2+</sup>	+ 1.8 V

The potentials for corresponding halogen reactions is + 2.055 V for fluorine, + 0.544 V for chlorine, and – 0.28 V for iodine. Thus, bromine reacts less vigorously with water than fluorine and chlorine.

When bromine itself becomes the reducing agent, bromide and hypobromite are formed during the partial disproportionation:



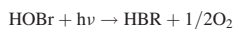
The equilibrium constant for this reaction is  $5.8 \times 10^{-9}$  at 25 °C and varies little with temperature [26]. This reaction can be suppressed by addition of acid. With a small amount of base, the reaction goes to completion. In strong base, the reaction occurs only in the cold. Warming under these conditions converts the hypobromite to bromate and bromide:

For sodium hypobromite, the reaction is:

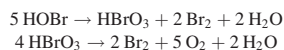


With the addition of acid to the bromate–bromide mixture, bromine is again formed.

Light is known to catalyze the decomposition of HOBr to hydrogen bromide and oxygen as follows:



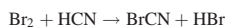
In the dark, HOBr decomposes to bromic acid and bromine. Bromic acid is relatively unstable and undergoes slow decomposition to produce bromine and oxygen. This sequence is given by the following reactions:



For  $\text{Br}_2$ , its equilibrium concentration in aqueous solution at 25 °C is as follows [27]:

Total solubility	0.21 mol/L
$\text{Br}_2$ concentration (aqueous)	0.21 mol/L
$[\text{H}^+] = [\text{Br}^-] = [\text{HOBr}]$	$1.15 \times 10^{(3)} \text{ mol/L}$

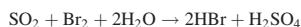
Bromine reacts with *hydrogen cyanide* to produce cyanogen bromide:



Carbonates react with bromine, forming bromide and bromate salts:

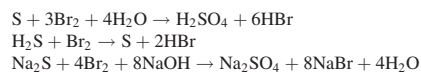


Sulfur dioxide is oxidized to sulfuric acid by bromine:

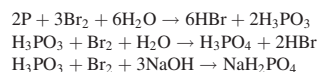


The latter two reactions are used commercially in recovering or neutralizing bromine residues.

Bromine also oxidizes elemental *sulfur*, hydrogen sulfide, and sodium sulfide as described by the following reactions:

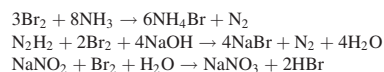


It is also known that bromine reacts with red *phosphorus* and other phosphorus compounds according to the following reactions:



*Nitrogen-containing compounds*, e.g., ammonia, hydrazine, nitrites, and azides also undergo oxidation by bromine, with elemental nitrogen as the frequent product from such reactions.

The reactions of ammonia and other nitrogen-containing compounds with bromine to form nitrogen or nitrate are as follows:



Bromine reacts directly with *hydrogen* ( $\text{H}_2$ ) at higher temperatures to form hydrogen bromide, a reaction which is the basis for the commercial production of HBr. Catalysts for this reaction include heated charcoal and finely divided platinum metal.

Bromine also reacts with many *metals* to form bromides. Sodium is stable in dry bromine, but sodium vapor reacts vigorously. Potassium and cesium react violently with bromine. Bromine is also highly reactive with aluminum and titanium. Aluminum reacts

with the emission of light. Magnesium, silver, nickel, and lead become coated with their bromide, which prevents further reaction. This protective coating makes lead a useful material for containers to hold bromine. Other non-ferrous metals, that are useful in handling bromine are nickel, tantalum, Hastelloy C, and monel and certain other copper alloys.

Moisture is important in the corrosion of metals by bromine. This is probably due to the hydrolysis products, hydrobromic and hypobromous acids. At moisture contents below 40 ppm, nickel containers can be used for transporting bromine [28]. Mercury is attacked by bromine and should not be used in instruments and gages exposed to bromine vapor. Dry bromine reacts slowly with iron to form a protective layer of ferric bromide; but when wet, a mixture of hydrated iron bromides is formed which does not adhere to the iron surface [29]. Other heavy metals, such as copper, manganese, chromium, antimony, cobalt, cadmium, and bismuth, react with bromine, although some metals require higher temperature.

Bromine also reacts with plutonium and uranium and offers the possible separation of  $\text{UBr}_4$  and  $\text{PuBr}_3$  by distillation. Titanium and zirconium are said to form  $\text{H}_2\text{TiBr}_6$  and  $\text{H}_2\text{ZrBr}_6$  in solution [30]. Bromine also reacts with some metal oxides, e.g., thorium oxide, at high temperature in the presence of reducing agents to form bromide.

### 3.1. Bromine Addition to Alkenes and Alkynes

Bromine adds readily to unsaturated compounds [31, 32]. Such reactions are usually run at low temperature to avoid substitution side reactions. Although a catalyst is usually not required, ultraviolet radiation or high temperature may be used to accelerate the reaction.

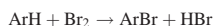
Among the more important commercial products from bromine addition to unsaturated compounds are ethylene bromide, acetylene tetrabromide, 2,3-dibromopropanol, hexabromocyclodecane, and tetrabromobisphenol A bis(2,3-dibromopropyl ether) ( $\rightarrow$  Bromine Compounds).

### 3.2. Bromination of Aromatic Compounds

Aromatic compounds can undergo three types of reactions with bromine: (1) addition, (2) substitution on side chains, and (3) substitution on the aromatic ring.

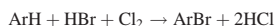
The light-catalyzed addition of bromine across aromatic double bonds is generally a slow reaction, but use of chlorine increases the rate. Bromination of aromatic side chains is normally a free-radical process.

Electrophilic substitution on the aromatic ring is by far the most important type of aromatic bromination. In the presence of a catalyst, bromine reacts with aromatic compounds to give aryl bromides and hydrogen bromide:



Suitable catalysts for aromatic brominations are Lewis acids, such as halides of aluminum, iron, zinc, or antimony. Activated aromatic compounds, such as phenols, anilines, and aromatic ethers, can be brominated without a catalyst. In contrast, very strongly deactivated aromatic compounds containing electron-withdrawing groups, undergo bromination in the presence of sulfuric acid in combination with nitric acid [33].

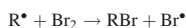
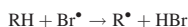
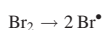
Bromine in situ generated from hydrogen bromide is more efficiently used in aromatic substitution:



Preformed bromine chloride can also be used for the same purpose. Substitution reactions involving  $\text{BrCl}$  are much faster than ones using bromine alone [34].

### 3.3. Free-Radical Bromination

Bromination of saturated hydrocarbons and of alkyl side chains of aromatic compounds occurs by a free-radical chain reaction:

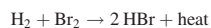




Dissociation of bromine molecules is needed to initiate this reaction. Bromine can be dissociated thermally, photolytically, by gamma radiation, or by use of peroxide initiators. Compared with chlorine, the bromine atom is less reactive and the hydrogen abstraction step is endothermic. As a result, reaction rates are relatively slow and the bromine atom exhibits high position selectivity. For example, in bromination of *n*-butane, secondary hydrogen atoms are replaced 82 times faster than primary ones [35]. Bromination of aromatic side chains is a much faster reaction than bromination of alkanes.

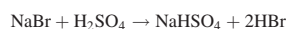
### 3.4. Production of Hydrogen Bromide

Hydrogen bromide [10035-10-6] is an important intermediate in producing various organic and inorganic bromides ( $\rightarrow$  Bromine Compounds). The intermediates find applications in the production of medicinals, dyes, perfumes, photographic chemicals and many other chemistries. Hydrogen bromide is prepared commercially by the direct gas-phase reaction of hydrogen and bromine:



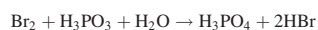
The reaction can be conducted without catalyst by maintaining a self-sustaining flame within an enclosed burner [36].

Hydrogen bromide may be prepared in the laboratory by distilling a solution of sodium or potassium bromide with phosphoric acid or dilute sulfuric acid (5.8 M). For sodium bromide as the starting material:



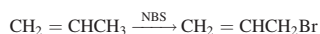
Using more concentrated sulfuric acid or allowing the reaction solution temperature to go above 75 °C is not effective as the HBr initially formed will be oxidized to gaseous bromine ( $\text{Br}_2$ ) [37].

Another laboratory HBr preparation method is based on the reduction of bromine with phosphorous acid:



### 3.5. Bromination Using Bromine Carriers

Bromine complexes and bromoimides are useful for brominations where selectivity is of prime importance. The bromine carrier that has found the most use in laboratory brominations is *N*-bromosuccinimide (NBS) [128-08-5]. A unique application of NBS is in free-radical allylic brominations:

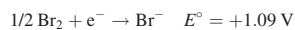


Other useful bromine carriers are dibromodimethylhydantoin, dioxane dibromide, pyridine hydrobromide dibromide, and various quaternary ammonium polybromides [38].

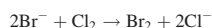
## 4. Production

Bromine production utilizes bromine-containing liquors (brines), which occur naturally, or result from the manufacture of potassium salts or from seawater.

In most brines, as well as in ocean water, the molar concentration of chloride ions is likely to be 200 to 700 times as large as that of bromide ions. Therefore, isolating bromine from these sources requires a separation method of high selectivity. Fortunately, such a method exists. It is based on the greater ease with which bromide can be oxidized compared to chloride, and the fact that the oxidation product, bromine, is quite volatile. Chlorine [7782-50-5] serves as the most economical and convenient oxidant. The normal oxidation–reduction potentials ( $E^\circ$ ) applicable to the operation are:



Overall reaction:



There are 4 principal stages in bromine production:

#### 1. Oxidation of bromide to bromine



2. Stripping of bromine from the aqueous solution
3. Separation of bromine from the vapor
4. Purification of the bromine

Two general processes using chlorination for bromine recovery are based on the above chemical reaction:

- Steaming-out process for brines and waste liquors containing bromine. Steam is employed when the bromide concentration in the brine is above 1000 ppm. The advantage of this process is that bromine can be condensed directly from the steam.
- Blowing-out process for seawater. Air is used when seawater is the source of bromine because very large volumes of stripping gas are required and steam would be too expensive. When air is used, it is necessary to trap the bromine in an alkaline or reducing solution to concentrate it.

The composition of typical brines arriving at an Arkansas bromine plant is 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 and 0.01–0.02 g/L

iodide. These brines may contain in addition some dissolved organics including natural gas and crude oil. The bromide-containing brine is initially treated to remove natural gas, crude oil and hydrogen sulfide before its introduction into the contact tower.

For bromine production in Israel, an average composition of liquors exiting Dead Sea potash production and used then as the raw material for bromine was the following (2001): 45 g/L Ca, 85 g/L Mg, 350 g/L chloride, and 12 g/L bromide.

#### 4.1. Steaming-Out Process

Production of bromine from brines containing  $\text{Br}^-$  in concentrations of 1–5 g/L basically follows the process described by KUBIERSCHKY in 1906 [39].

Raw brine is warmed in a heat exchanger (a) and caused to pass successively through two packed towers (b), (c) by gravity flow (Fig. 5). In the upper (smaller) tower, it meets a recycle stream of gases from which chlorine and bromine are absorbed. Near the bottom of the lower tower (c), chlorine and steam are introduced; as they pass upward, the chlorine reacts

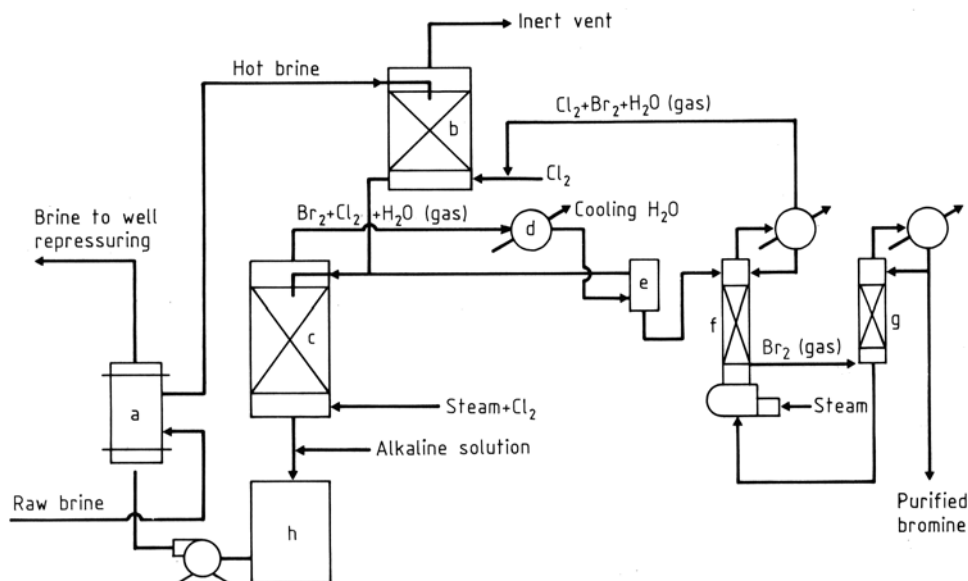


Figure 5. Bromine steaming-out process

a) Bromine cross heat exchanger; b) Chlorine absorber; c) Steaming-out tower; d) Condenser; e) Separator; f) Stripping column; g) Fractionating column; h) Neutralizer

with bromide in the brine, and a mixture of bromine vapor and chlorine (about 85: 15 by weight) with steam is taken off the top. The water and most of the halogens are condensed (d), the liquid phases enter a gravity separator (e) and the gas goes to the upper tower. From the separator, water containing dissolved halogens is sent to the lower (steaming-out) tower and the heavier bromine layer, containing some chlorine, flows to a fractionating column (g). The chlorine vapors join the stream to the upper tower while the liquid bromine, about 99% pure, is drawn off either for direct use in the manufacture of bromine compounds or to be further purified for sale or for more exacting uses.

The hot debrominated brine is treated to neutralize acidity (h) and to reduce free halogens, if necessary, and then is passed through the heat exchanger, where it warms the incoming brine.

More recent modifications of the original Kubierschky process are related generally to the larger scale of modern operations, to the materials of construction, which must be corrosion resistant, and to the procedures and instrumentation needed for control. Whereas originally most of the construction was stone-ware, brick, or lead, now much of the material exposed to wet halogens is glass, tile, or other special ceramics or alloys and fluoropolymers; tantalum may be used for condensers [40]. The processes are controlled by measuring pH, oxidation–reduction potentials, flow rates, temperatures, and pressures at critical points.

Some acidity is generated when chlorine reacts with reducing substances, such as hydrogen sulfide, in the brine. This acidity adds to the efficiency of bromine liberation by preventing hydrolysis to hypobromous acid. Use of sulfuric acid is not advisable if the brine contains calcium or strontium because they may precipitate as sulfates and foul the tower packing, heat-exchange surfaces, or brine disposal wells. However, sulfates will form if the brine contains sulfides.

## 4.2. Seawater Process

The first economically successful recovery of bromine directly from the sea was carried out

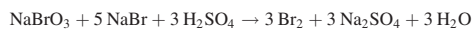
near Wilmington, North Carolina (USA), using an *air-blowing process* originally developed for brine operations by H. H. Dow [41]. The use of air rather than steam is necessary because the cost of steam to heat ocean water, with its bromine content of only about 65 mg/L, would be prohibitive. The Wilmington plant has since been abandoned.

Water from the ocean is pumped to the top of blowing-out towers, with sulfuric acid and chlorine being added just above the pumps so that mixing takes place during the ascent. About 1.3 kg of 10% sulfuric acid per ton of water is required to neutralize the natural hydrogen carbonates and bring the pH to 3.5; 15% excess chlorine over the theoretical requirement is used [42].

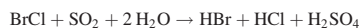
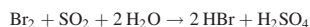
Air is drawn up through the towers, sweeping out a mixture of bromine and chlorine (or bromine chloride) from the descending ocean water. The air is drawn next through absorber towers in which it is scrubbed counter-currently by sodium carbonate solution. The several reactions which take place may be summarized approximately by the equation:



To remove spray from the air, small packed chambers are interposed between the absorber towers and the fans. When the alkalinity of the scrubber solution is nearly depleted, the solution is brought first to a storage tank and then to a reactor in which it is treated with sulfuric acid and steamed out to release bromine:



In a modification of the process [43, 44], which was used for a number of years at Freeport, Texas, halogens blown from the ocean water are reduced with sulfur dioxide and absorbed in a water spray:



The resulting aqueous solution of mixed acids is treated with chlorine in a conventional steam-out tower and the bromine is recovered.

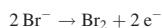
The mixture of hydrochloric and sulfuric acid remaining is used for acidifying the raw ocean water.

Because of the large volume of ocean water processed, the bromine-depleted stream must be discharged at some distance from the intake and in a favorable location from the standpoint of prevailing currents, to avoid dilution. Aside from this, *waste disposal* is not a problem since both the acidity and the free halogen content of the outgoing water are very low. In contrast, the waste stream from a strong brine process requires neutralization and, in some instances, reduction. In most cases, spent well brine is returned to the ground by means of disposal wells to maintain hydrostatic pressure within the formation. Acidity or free halogens should be absent to minimize corrosion of the system. Lime or caustic soda are customarily used for neutralizing acidity. The use of semi-burnt dolomite with sodium thiosulfate has been recommended [45].

*Analytical methods* used for bromide in brines and ocean water have been described [46]. Usually the van der Meulen method [47] or one of its various modifications is employed. *Economic factors* important in the location of seawater bromine plants, especially as they were related to the siting of the Amlwich operation (in the UK), have been discussed [48]; temperature of the water has a significant effect on the efficiency of the blowing-out process [49].

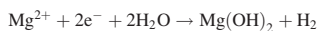
### 4.3. Electrolysis

Electrolysis was used in early production in Germany instead of chlorine to oxidize bromides. Two processes were developed in Germany. The *Wunsche electrochemical process* was based on the use of diaphragms to provide good current efficiency. The carbon cathodes were separated from the carbon anodes by porous clay cylinders, which allowed ion diffusion. The anode reaction product was bromine:



The cathode reaction produced hydrogen and magnesium hydroxide, which created a

major problem of clogging the clay diaphragm pores:



The *Kossuth electrochemical process* used bipolar carbon plate electrodes with one side serving as anode and the other side as cathode. The power supply was connected to the end electrodes, and to dislodge the magnesium hydroxide deposits that built up on the cathodes, the current was periodically reversed for a short time. Despite this advantage over the Wunsche process, the Kossuth process had very low-current efficiency. The amount of power required related to bromine was 3000 kW h/t as compared to about 2000 kW h required to produce 500–600 kg of liquefied chlorine used to make 1 t of bromine by the Kubierschky process (Section 4.1.), which was being developed at the same time.

Current bromine production methods are based on modified Kubierschky or steaming-out processes and Dow Chemical's blowing-out process.

As the transportation and storage of liquid bromine of the liquid bromine must satisfy very strict requirements, it has been realized that there is a need in various industrial plants that utilize molecular bromine for an in-situ generation of  $\text{Br}_2$  using a safe method. Two possibilities for such methods are outlined below:

1. A process [50] in which hydrogen bromide may be oxidized to bromine more effectively using hydrogen peroxide (30–50%) as the oxidizing agent if a strong acid such as sulfuric or phosphoric acid is also present to raise the percent conversion of bromide to bromine. The temperature is in the range of 20–55 °C. The strong acid/bromide ratio ranges from 0.6–2 moles acid to 1 mole of bromide. The bromine fraction is distilled in the final step.
2. A process [51] which generates gaseous bromine is based on the oxidation of an aqueous bromide ion solution in an acidic environment at temperature of between 59 °C and the boiling point of the aqueous reaction mixture to produce molecular bromine in the gaseous state. A stream of inert

gas, e.g., air, is passed through the reaction zone with the aim of removing bromine vapors from the reaction zone. When sodium bromate is the oxidant, the reaction is the following:



#### 4.4. Bromine from Recycle and Waste Brines

In the United States, a modified Kubierschky process has been used for recovering bromine as a byproduct from potassium chloride production liquors at Searles Lake [52]. The Searles Lake brine contains ca. 0.085% bromine, but it is too alkaline and too heavily buffered for direct use in the conventional chlorine process of liberating bromine. However, since potassium bromide and potassium chloride are isomorphous, the bromide crystallizes with the potassium chloride. This mixture, containing up to 1.8% bromide, is neutral and therefore useable. When chlorinating this mixture, the bromine is expelled and recovered while an equivalent amount of new potassium chloride replaces the bromide and thus effects the desired purification of the chloride product.

For economic reasons, increasing attention is being given to the development of methods for recovering bromine from byproduct bromides, such as those obtained in halogen displacement reactions. Many substitution reactions using bromine produce a kilogram of bromine in the form of byproduct hydrogen bromide for each kilogram of bromine substituted in the desired product. The hydrogen bromide, which is usually released as a gas, is absorbed into water or in an alkaline solution using a scrubber. The aqueous scrubber effluent is acidified and chlorinated in order to recover the bromine for recycle. In some cases, the hydrogen bromide is recovered and used as is or as the bromide salt in other applications.

Plastics containing brominated fire retardants (BFRs) can be incinerated as a solid organic waste, and the bromine can be subsequently recovered. Trials conducted at the TAMARA pilot scale municipal solid waste combustion (MSWC) facility (5 t/d) in the Karlsruhe Research Centre (Germany)

have demonstrated that in modern MSWC plants equipped with suitable wet scrubbing systems, recycling of the bromine in plastics waste containing brominated flame retardants is technically feasible [53]. Different types of commercial bromine-based finished products can be produced, including bromine itself, hydrogen bromide or sodium bromide. Plant operation was carried out at about 1000 °C, in the upper range of temperatures used in standard municipal waste treatment facilities.

A more recent study [54] reported on the thermal degradation behavior of electronic boards manufactured using tetrabromobisphenol A and diglycidyl ether of bisphenol A epoxy resins. Qualitative and quantitative information was obtained concerning the products formed in the thermal degradation products. Also the bromine distribution in the different product fractions were determined. The more important decomposition products included HBr, phenol, polybrominated phenols, and polybrominated bisphenol A species.

#### 4.5. Purification

Bromine produced by either the steaming or blowing processes ordinarily contains as impurities chlorine, water, halogenated hydrocarbons, and acids (HCl or HBr). Fractional distillation brings the purity to 99.5–99.7%, long associated with commercial bromine. Improvement to the 99.9+ quality available at present may be done by proprietary methods, of which the following may be considered representative.

Maintaining bromine at 50 °C for 4 h with provision for removal of the vapor lowers the chlorine content from 0.12 to 0.06% and moisture from 0.05 to 0.005% [55]. Passing predried, vaporized bromine and oxygen through a tube packed with quartz or Vycor glass fragments and heating to 1000 °C decomposes organic halogen compounds, such as chloroform [56]. Heating bromine vapor to 370–540 °C decomposes organic impurities to HCl and to higher boiling compounds which can be removed by distillation [57]. A mixture of steam and bromine can be heated to similar temperatures. Upon cooling, the impurities remain largely in the aqueous phase [58].

Absorption of bromine by a bromide solution with subsequent steam stripping provides highly purified bromine with essentially no chlorine [59].

To avoid corrosion of lead, nickel, or Monel containers, less than 30 ppm water should be present in bromine. Drying with concentrated sulfuric acid removes most of the moisture. Organic impurities can be removed by distilling bromine at 58 °C with 96% sulfuric acid, ca. 2 L/1000 kg, washing the condensed bromine with water, and drying counter-currently with 98% acid [60]. In addition drying can be done with molecular sieves, type 3 A–5 A (0.3–0.5 nm) [61]. The laboratory preparation of extremely pure bromine for physical properties determination has been described [62].

A newly patented process [63] for drying liquid bromine utilizes 2 fractionators to produce a substantially dry liquid bromine stream and a substantially bromine-free water stream. In the process, wet bromine liquid may be conveyed to a first fractionator in which a substantially dry bromine is produced. A vapor stream from the first fractionator may be condensed into a first liquid phase comprising bromine saturated with water and a second liquid phase composed of water saturated with bromine. This second phase may be conveyed to a second fractionator to produce at least substantially bromine-free water.

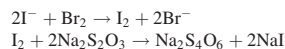
## 5. Quality Specifications and Testing

Typical industrial product specifications for purified bromine are:

Bromine, min.	99.98%
Chlorine, max.	100 ppm
Water, max.	30 ppm
Nonvolatile residue, max.	30 ppm
Organics, total identifiable, max.	100 ppm
Specific gravity, 20 °C	3.12

Bromine and bromine compounds can be analyzed by methods found in [64]. Liquid bromine and bromine solutions can be assayed by standard iodometric titration [65]. An ampule of bromine is crushed beneath the surface of an aqueous potassium iodide and

the resulting liberated iodine is titrated using a standard potassium thiosulfate solution.



Bromine vapor can be analyzed by absorption in aqueous potassium iodide solution and the liberated iodine is also titrated iodometrically. A modification of this procedure uses a spectrophotometer to measure the iodine concentration by determining the absorption of the triiodide ion formed by addition of excess iodide [66].

The specific gravity of liquid bromine can be determined by a hydrometer.

### 5.1. Qualitative Methods for Bromine and Bromides

- Bromine, at higher concentrations, forms colored solvents such as carbon tetrachloride or carbon disulfide.
- Bromine reacts with yellow disodium fluorescein [518-47-8] to form red disodium tetrabromo-fluorescein (eosin) [548-26-5]. As little as 0.3 µg bromide can be detected without interference from chlorides.
- Bromine reacts with platinum sulfate [7446-29-9] solution to form red-brown crystals of potassium hexabromoplatinate [16920-93-7].

### 5.2. Quantitative Methods for Bromides

- Mohr method: Use of titrant and potassium chromate indicator.
- Volhard method using excess titrated with potassium thiocyanate and ferric ammonium sulfate indicator.
- Fajans method using silver nitrate as titrant, eosin as absorption indicator.
- Silver nitrate titrant with potentiometric determination of endpoint.
- Silver nitrate gravimetric method.
- Bromides in acidic solutions using a titration with mercuric iodide using sodium nitroprusside indicator.



Some of the methods used for determining trace amounts of bromide quantitatively include [67]:

- Van der Meulen method useful in presence of large chloride concentrations.
- Constant-current and constant-potential coulometry, capable of determining fractions of a milligram to several grams of bromide.
- Ion chromatography.
- Polarography for microgram quantities.
- Spectrophotometric methods useful for microgram quantities in the presence of chlorides.
- Neutron activation analysis for nanogram quantities.

A method for the separation of iodide, bromide, and chloride ions in any mixture involves selective oxidation and distillation, followed by potentiometric or spectrophotometric determination. Other methods for analyzing mixtures of halide ions include chromatography and precipitation.

Various procedures are used for the analysis of impurities in bromine. For example, chlorine content ( $\eta$ ) in bromine can be calculated (in wt%) by accurately measuring its density ( $\rho$ ) and temperature  $T$  (in K) and then using the formula:

$$\eta = 109.4 - 0.088234 T - 26.738 \rho$$

A more accurate and convenient method for chlorine determination is ion chromatography [68]. Pure bromine is transparent in the infrared, so water and organic impurities can be measured by their IR absorption spectrum. The residue after evaporation of bromine is determined by heating a sample in a tared container on a steam bath, drying at 105 °C, and weighing.

The bromine content in organic compounds can be determined by neutron activation, atomic emission spectroscopy, infrared spectroscopy, and X-ray fluorescence. The bromine content can also be determined chemically after oxidation of the organic compounds and reduction of bromine to bromide. When using the Schoniger method [69, 70], a few milligrams of sample are burned inside a stoppered Erlenmeyer flask filled with oxygen. Following

ignition by electrical or other methods, the combustion products are absorbed and the bromine content is determined. Another method uses fusion with sodium peroxide in a Paar bomb.

## 6. Storage and Transportation

Bulk quantities of bromine are usually shipped within the United States in 7570 and 15 140 L lead-lined pressure tank cars or 6435–6813 L nickel-clad pressure tank trailers [71]. The trailers must be filled at least 92% to capacity in order to prevent inertia effects of the heavy liquid while being transported on highways. International shipments by the Dead Sea Bromine Group are carried out in 15.2–23.3 t (5300–8000 L) lead-lined tank containers (isotanks). For smaller quantities of bromine, lead-lined tanks (goslars) of 3.5 t (4 tanks packed on a single isoframe) and 400 kg drums are used. Dry nitrogen is recommended for use in pressure-transferring bromine, although dry air may also be used. The gas that is used must be absolutely dry or else severe corrosion results, as discussed below. When exposed to a high-humidity atmosphere, the water content of bromine can exceed 300 ppm.

The relatively high freezing point of bromine (−7.25 °C) may cause some problems in storage and shipping. If there is evidence that the bromine is frozen, although the cars are usually insulated, warm water (below 54 °C) should be circulated through the heating coils. Steam should never be used, as bromine boils at 58.6 °C.

Storage tanks should be protected from moist air. Bromine that contains 30 ppm of water will pick up moisture from air having a dew point of −70 °C. Bromine in equilibrium with air having a normal summer dew point of 5–10 °C contains about 70 ppm of water. Corrosion of many bromine-handling metals is severe at this concentration of water. To keep out moisture, a very slight positive pressure (25 Pa) should be kept on bromine storage tanks by purging dry nitrogen or dry air into the tank vent line just above its connection to the tank. When pressurization of the tank is necessary for unloading, dry air should be used, and no more



pressure applied than is required to lift the bromine to the highest point in the unloading system (7 kPa gauge pressure lifts bromine 0.23 m).

For transferring bromine, plastic-lined steel is a versatile material that combines chemical resistance with reinforced strength. Fluorinated plastics, such as Kynar, Teflon, Kel-F, and Viton, find widespread use in equipment, valves, piping, and gaskets. Nickel, Monel alloys, and Hastelloy C alloys may be used with dry bromine (less than 30 ppm water) but are severely attacked by wet bromine. Tantalum may be used with either wet or dry bromine up to 150 °C. Steel and stainless steel usually are unsatisfactory. However, the use of steel is possible when nitric oxide is present to prevent corrosion. Chemical lead- and glass-lined steel are probably the most versatile and practical materials for general use in storing and handling bromine.

Because of the hazards involved in the transporting and storing liquid bromine, the idea of using a bromine carrier has been considered by many over the years. The idea would involve using a salt possessing a high concentration of bromine (the salt being made using bromine) and shipping it either as a concentrated solution or as a solid to customers. It would be necessary for customers to build a small bromine generator on their site, based on the reaction of chlorine gas with bromide to release bromine. This scenario may be attractive for customers having their own chlorine source or who are located near a chlorine manufacturer. Calcium bromide ( $\text{CaBr}_2$ ) would seem to be the best choice as it contains about 80 wt% of bromine. Another possibility might be magnesium bromide which contains about 85 wt% bromine. Disadvantages to the idea of this type of bromine are:

- The added cost of making the carrier from elemental bromine.
- The need to prepare bromine in situ.
- The necessity to ship chlorine (if the customer does not have any of its own), which creates a greater hazard than bromine itself.

Until the present (2014), there has been no commercial use of such bromine carriers.

## 7. Uses

The major uses of bromine in terms of consumption are in flame retardants, drilling fluids, organic synthesis, pharmaceuticals, biocides for water treatment, and agriculture (Table 9). Bromine is also used in the manufacture of dyes, insect repellents, perfumes and photographic materials. Other bromine compounds find uses in other applications including mercury control and paper manufacturing.

Brominated flame retardants are the most voluminous and significant part of bromine derivatives ( $\rightarrow$  Flame Retardants). Bromine consumption in flame retardants has risen substantially since the early 1990s and in 2013 formed more than half of total bromine consumption [72]. Brominated flame retardants are used in industrial and domestic equipment such as computers, furniture, boards, mobile phones, televisions, and textiles. More than 90 different aliphatic, aromatic, and polymeric compounds have been registered as brominated flame retardants. Some of these chemical classes include brominated phenols, bisphenols, diphenyl ethers, polystyrene, polyacrylates and epoxy oligomers [73]. Manufacturers introduce new brominated flame retardants continually, some compounds are banned from the market because of environmental concerns. In 2010 US bromine chemical producers and importers reached an agreement with the US Environmental Protection Agency to voluntarily phase out the production, importation, and use of decabromodiphenyl ether in all consumer products by December 2012, and in all products by the end of 2013.

The high-density characteristics of bromine compounds are advantageously applied in hydraulic fluids, gage fluids, ore flotation, and drilling fluids. The oil and gas drilling industry uses calcium, zinc, and sodium

**Table 9.** World bromine and bromine compounds consumption in 2013 [72]

Consumer segment	Consumption, t
Flame retardant	483 000
Drilling fluids	103 500
Organic synthesis	86 300
Pharmaceuticals	77 600
Water treatment	69 000
Agriculture	43 100

bromides to prepare high-density, clear brine drilling, completion, packer, and workover fluids [74]. For such applications, calcium bromide is the largest volume bromide salt in use, followed closely by zinc bromide and sodium bromide. Calcium bromide, 52% aqueous solution, was introduced in 1972 as a dense fluid product (1.70 kg/L) for use as oil well packs and completion fluids [75]. The use of calcium bromide, zinc bromide, and sodium bromide as completion fluids in oil and gas well drilling has grown rapidly over the years since their introduction. These high-density fluids also help in preventing migration of fluids between underground formations through the well bore.

With bromide pricing increasing rapidly over the last few years, customers and service companies have begun to reclaim these clear brine fluids to save money and eliminate disposal costs for the used brines (in particular zinc bromide) resulting in a mix of 35–45% virgin clear brine fluids (CBFs) and 55–65% reclaimed fluids.

Bromine use in CBFs is known to be highly dependent on fluctuations in the oil and natural gas drilling industry. Thus CBF consumption in crude oil and natural gas drilling has been expected to increase as demand for these commodities increase. Expectations for drilling increasingly deep and high-pressure oil and gas formations, especially employing deep water hydraulic fracturing techniques, increases the probability for greater demand for CBFs.

A significant and expanding group of brominated biocides is for water treatment [76] (→ Biocides). While chlorine controls the majority of the water-treatment markets, brominated compounds are becoming increasingly popular. In general, both industrial and consumer segments of the water-treatment industry are increasingly replacing chlorine and chlorinated compounds, such as sanitizers and biocides, with bromine-based products. Chlorine is now subject to a wide range of EPA limitations, and although bromine is itself a halogen, no restrictions have yet been placed on brominated biocides. In addition, the greater strength of bromine-based biocides allows treatment of a given amount of water with considerably less biocide. This not only reduces the amount of halogen released into the environment, but can

also reduce costs for municipal and industrial water treatment plants. Benefits accrue through reduced chemical costs, avoidance of the dechlorination step common in chlorine water treatment, and reduced corrosion to condensers, tubing and other equipment.

Brominated biocides also perform better than chlorinated biocides in a number of industrial applications because of their higher tolerance to a wide range of pH levels, a concern in cooling towers and process waters [77].

In addition, brominated biocides are more stable than chlorine in higher temperature waters, do not readily decompose on exposure to sunlight and are less irritating to the eyes and mucous membranes. This is particularly important in the recreational segment of the water treatment market. As a result, brominated biocides for water treatment will continue to expand their market share.

Bromomethane, a very active biocide was used as a space fumigant applied for killing soil parasites in agriculture and for sanitization of cereal and other crops under storage and before shipment. However, due to its role in depletion of the ozone layer, in 1997 at the Ninth Meeting of the Parties of the Montreal Protocol, the members agreed to a schedule for a reduction in the use of the fumigant and complete phase-out by 01.01.2015.

The use of bromine and bromine compounds to mitigate mercury emissions at coal-fired power plants has been a growth market for bromine producers [78–80]. Inorganic bromine compounds (calcium bromide and sodium bromide) bond with mercury present in flue gases from coal-fired power plants creating mercury compounds that are captured in scrubbers, thus removing as much as 90% of the mercury liberated during combustion. Tentative results have suggested that bromine only requires a fraction of the amount of chlorine required for the complete elimination of mercury. Tests by the Electric Power Research Institute project determined that bromine costs were only slightly higher than for chlorine for 500 MWh, but the reaction rate was approximately 8 times faster [81]. Wide acceptance of the new technology will likely increase demand of bromine, counteracting, at least in part, the decline expected from the ban of decabromodiphenyl ether and methyl bromide.

**Table 10.** World production and reserves of bromine [82]

Country	Production, t		Reserves, t
	2012	2013	
United States	Withheld to avoid disclosing company proprietary data. U.S. production 2006 (the latest record) was 243 000 t.		11 000 000
Azerbaijan	3500	3500	300 000
China	100 000	100 000	Not available
Germany	1500	1500	Not available
India	1500	1500	Not available
Israel	174 000	180 000	Not available
Japan	20 000	20 000	Not available
Jordan	200 000	250 000	Not available
Turkmenistan	150	480	700 000
Ukraine	4100	4100	Not available
World total excludes U.S. production	505 000	560 000	Large

## 8. Economic Aspects

World bromine production for 2012–2013 and distribution for each major producing country is shown in Table 10 [82]. The U.S. share of the world bromine production has decreased while other countries have improved their positions as world producers of elemental bromine. Thus, Israel, the U.S., Jordan, China, Japan, and Turkmenistan, in descending order, had the largest bromine capacities in 2012. None of these countries operated at capacity.

It has been estimated that between 40–50% of U.S. domestic consumption of bromine was for flame retardants. In 2012, demand for flame retardants, particularly in the construction and electronics industries, increased as the economy recovered from recession.

## 9. Toxicology and Occupational Health

**Bromine Vapor.** In the vapor state, bromine is similar to chlorine in physiological reactions, having a sharp, penetrating odor. As a result of its oxidizing action, comparatively low concentrations of bromine vapor are highly irritating to the entire respiratory tract, the mucous membranes, and the eyes, producing responses, such as coughing and smarting of the eyes. The approximate exposure limits for bromine vapor are given in Table 11.

The Occupational Safety and Health Administration (OSHA) threshold limit value-time-weighted average for an 8 h workday and 40 h work week is 0.1 ppm (in the air).

Exposure to high concentrations of Br<sub>2</sub> vapor leads to inflammation and congestion of the respiratory system and edema of the lungs, which in severe cases can be fatal. The sharp odor of bromine gives warning against acutely dangerous exposure but not against concentrations which may be harmful as a result of prolonged exposure.

**Liquid Bromine.** Bromine in the liquid state presents a serious hazard in handling. It rapidly attacks the skin and other tissues to produce irritation and necrosis; the burns are not only

**Table 11.** Exposure limits for bromine vapors [83–85]

	Vapor concentration, ppm
TLV:TWA	0.1 (0.66 mg/m <sup>3</sup> )
STEL	0.2 (1.4 mg/m <sup>3</sup> )
MAK	0.1 (0.66 mg/m <sup>3</sup> )
IDLH	3 (20 mg/m <sup>3</sup> )
Maximum allowable concentration that is tolerated without disturbance	
Prolonged exposure (several h)	0.1–1
Short exposure (<1 h)	4
Least detective odor	~3.5
Least amount causing irritation of the throat	10
Dangerous to live (short exposure)	30

painful but slow to heal. Liquid bromine can also cause severe eye damage.

For the average person, the ratio of bromine to chlorine is roughly about 1:100 in both blood and urine. Table salt has been implicated as the major source of dietary bromine, as it may contain as much as 0.1% (1000 ppm) bromide [86]. The World Health Organization in 1967 stated that the maximum acceptable daily intake of bromide ion is to be 1.0 mg/kg.

Acute bromide intoxication is rare because amounts sufficient to elevate the serum bromide to a toxic level can hardly be ingested and retained without vomiting. Chronic bromide intoxication from the continued use of large doses ( $> 3\text{--}5$  g/d) is known as bromism. The symptoms are skin rash, glandular excretions, gastrointestinal disturbances, and neurological disturbances. Bromide compounds have been used in the treatment of neurological disturbances as a sedative and in the control of epilepsy at doses of 3–5 g/d [87].

Dilute aqueous solutions of bromine exert considerable germicidal action; comparable studies suggest that it is commonly between chlorine and iodine in its activity against bacterial spores, although with some species, e.g., yeast and certain algae, it appears to be more toxic than chlorine. During disinfection, when ammonia compounds are present, the bromine (bromamine) species are much more toxic to microorganisms than are chlorine (chloramine) species [77, 88]. Also, the lower stability of bromamine residuals lowers their potential hazard to marine life by discharged effluents. In specific cases, the toxic action of bromine may well depend upon oxidation of enzyme functional groups, such as  $-\text{SH}$  and  $-\text{SS}-$ , or of the protein coat of the organism.

**Safety Precautions [89, 90].** Safe handling of bromine demands the following measures: (1) rigorous avoidance of all contact of bromine with skin, eyes, and clothing, and (2) adequate ventilation with all possible precautions against inhaling the vapors when significant quantities of bromine are to be handled. Good practice requires that goggles, face shield, gloves, and plastic or rubber suit be worn and that suitable gas masks be available. Preventative health measures and first-aid procedures are given elsewhere [16].

In the case of a bromine spill, all unprotected personnel should be evacuated from the area contaminated either by liquid or by vapor releases. Containment of the spill should be given first priority. Liquid bromine can be contained using earth, sand, or inert material. Vapors can be contained by covering the spill with water. Bromine can then be neutralized or decontaminated with potassium carbonate solution (10–50%), sodium carbonate, hydrogen-carbonate, or sodium thiosulfate (hypo). Anhydrous ammonia (in cylinders) is useful for neutralizing any bromine fumes. It is also useful in locating bromine leaks.

**Bromine Reactivity.** Bromine is non-flammable, but can ignite upon contact combustible materials, such as dry grass. The handling of bromine either in a wet atmosphere, or in extreme heat, or at temperatures low enough to solidify bromine (below  $6^\circ\text{C}$ ) should be strictly avoided. Bromine should be stored in a cool, dry area away from heat. Materials that should be prevented from coming into contact with bromine include combustibles, liquid ammonia, aluminum, titanium, mercury, sodium, potassium, and magnesium metal. Bromine is also known to attack some types of plastics, rubbers, and coating.

## References

- 1 A.J. Balard, *Ann. Chim. Phys.* **2** (1826) no. 32, 337.
- 2 C. Löwig: *Das Brom und seine chemischen Verhältnisse*, Heidelberg 1829.
- 3 G. Schwedt, *CLB Chemie in Labor und Biotechnik* **54** (2003) no. 3, 92–95.
- 4 G.W. Grubble: *Naturally Occurred Organohalogen Compounds – A Comprehensive Update*, Springer, Berlin 2010.
- 5 D.J. Faulkner, *Tetrahedron* **33** (1977) 1421–1443.
- 6 S. Enami et al., *J. Phys. Chem. A* **36** (2007) no. 111, 8749–8752.
- 7 R. von Glasow et al., *Atmos. Chem. Phys.* **4** (2004) 2481–2497.
- 8 M. Hausmann, U. Platt, *J. Geophys. Res.* **99** (1994) 25399–25413.
- 9 K. Hebestreit et al., *Science* **283** (1999) 55–57.
- 10 H. Leser, G. Honninger, U. Platt, *Geophys. Res. Lett.* **30** (2003) 1537.
- 11 N. Bobrowski, G. Honninger, B. Galle, U. Platt, *Nature* **423** (2003) 273–276.
- 12 “Bromine,” *Gmelin Handbook of Inorganic Chemistry, Supplement Volume A*, Springer, Berlin 1985, pp. 247–256.
- 13 A.J. Downs, C.J. Adams in A.F. Trotman-Dickenson (ed.): *Comprehensive Inorganic Chemistry*, vol. 2, Pergamon Press, New York 1973, p. 1107.

- 14 F. Yaron in Z.E. Jolles (ed.): *Bromine and its Compounds*, Ernest Benn Ltd., London 1966, pp. 43–49.
- 15 V.A. Stenger, *Angew. Chem. Int. Ed. Engl.* **5** (1966) no. 3, 280.
- 16 Dow Chemical, Bromine – Unloading, Storing, Handling, Form No. 101-2-80, 1980.
- 17 B.J. Karsten, *Z. Anorg. Allg. Chem.* **53** (1907) 379.
- 18 H. Stephen, T. Stephen (eds.): *Solubilities of Inorganic and Organic Compounds*, vol.1, Part 1, Pergamon, Oxford 1963, p. 93.
- 19 J. d'Ans, P. Hofer, *Angew. Chem.* **47** (1934) 71.
- 20 M.V. Stackelberg, *Naturwissenschaften* **36** (1949) 327.
- 21 M. Berthelot, *Ann. Chim. Phys.* **6** (1886) no. 7, 413.
- 22 A. Seidell in W.F. Linke (ed.): *Solubilities of Inorganic and Organic Compounds*, 3rd ed., vol. 1, Van Nostrand, Princeton, N.J., 1940, pp. 207–209.
- 23 A. Seidell in W.F. Linke (ed.): *Solubilities of Inorganic and Organic Compounds*, 4th ed., vol. 1, Van Nostrand, Princeton, N.J. 1958, pp. 440–444.
- 24 A.I. Popov in V. Gutman (ed.): *Halogen Chemistry*, vol. 1, Academic Press, New York 1967, p. 225.
- 25 N.N. Greenwood, A. Earnshaw: *Chemistry of the Elements*, 2nd ed., Butterworth-Heinemann, London 1997, p. 830.
- 26 H.A. Liebhafsky, *J. Amer. Chem. Soc.* **56** (1934) 1500; **61** (1939) 3513.
- 27 F.A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, 5th ed., Wiley Interscience, New York, 1988, p. 565.
- 28 D.E. Lake, A.A. Gunkler, *Chem. Eng. (New York)* **67** (1960) 136.
- 29 N.W. Gregory, B.A. Thackery, *J. Am. Chem. Soc.*, **72** (1950) 3176.
- 30 J.R.M. Fernandez, A.B. Duran, *An. R. Soc. Esp. Fis. Quim. B* **55** (1959) 823; *Chem. Abstr.* **54** (1960) 1800.
- 31 E. Schaumann (ed.): “Science of Synthesis”, *Houben-Weyl Methods of Molecular Transformations*, vol. 35, George Thieme, Stuttgart 2007, pp 439–493.
- 32 M. Eisen, D. Lenoir, *Chem. Eur. J.* **14** (2008), 9830–9841.
- 33 A.M. Andrievsky, M.V. Gorelik, *Russ. Chem. Rev.* **80** (2011) no. 5, 443–451.
- 34 J.F. Mills, J.A. Schneider, *Ind. Eng. Chem. Prod. Res. Dev.* **12** (1973) no. 3, 160–165.
- 35 P.C. Anson, P.S. Fredericks, J.M. Tedder, *J. Chem. Soc.*, Part 1, 1959 918.
- 36 Dow Chemical, US2070363, 1937 (J.C. Kur).
- 37 G. Brauer: “Chlorine, Bromine, Iodine”, *Handbook of Preparative Inorganic Chemistry*, 2nd ed., vol. 1, pp. 282–285.
- 38 R.H. Vekariya, H.D. Patel, *Tetrahedron* **70** (2014) 3949–3961.
- 39 K. Kubierschky, DE194657, 1906; *Z. Chem. Apparatenkd.* **3** (1908) 212; *Chem. Zentr.* **1** (1908) 2115.
- 40 F. Yaron in Z.E. Jolles (ed.): *Bromine and its Compounds*, Ernest Benn Ltd., London 1966, pp. 3–42.
- 41 Dow Chemical, US460370, 1891.
- 42 L.C. Stewart, *Ind. Eng. Chem.* **26** (1934) 361.
- 43 Dow Chemical, US2143223, 1939.
- 44 Dow Chemical, US2143224, 1939.
- 45 H. Kloth, B. Peter, *Bergakademie* **22** (1970) no. 10, 628.
- 46 J. Haslam, G. Moses et al., *Analyst. (London)* **75** (1950) 343, 352, 357, 371, 383.
- 47 J.H. van der Meulen, *Chem. Weekbl.* **28** (1931) 238.
- 48 H. Fossett, *Chem. Ind. (London)* 1971 no. 41, 1161.
- 49 C.M. Shigley, *J. Metals* **3** (January, 1951) 25.
- 50 Akzo American Inc., US5266295, 1993 (H.J. Barda).
- 51 Dead Sea Bromine Compounds, US 2012/0070365, 2012 (M. B. Freiberg, A. Meirum, D. Kopel, S. Shmilowitz, N. Faza).
- 52 G.R. Robertson, *Ind. Eng. Chem.* **34** (1942) 133.
- 53 APME + Forschungszentrum Karlsruhe + EBFRIP, *APME Report 8040* (2002).
- 54 F. Barontini et al., *Ind. Eng. Chem. Res.* **44** (2005) no. 12, 4186–4199.
- 55 VEB Kombinat Kali, US3615265, 1971 (R. Gartner).
- 56 U.S. Dept. of Army, US2929686, 1960 (M. Codell, G. Norwitz).
- 57 Michigan Chemical, US3314762, 1967 (L.H. Hahn).
- 58 Michigan Chemical, US3642447, 1972 (L.H. Hahn, C.W. Dunbar).
- 59 Great Lakes Chemical, US3145084, 1964 (L.R. Belohlav).
- 60 Kali u. Salz GmbH, DE2034437, 1972 (R. Sell, O. Braun).
- 61 Kali u. Salz GmbH, DE2034438, 1972 (R. Sell, G. Budan).
- 62 M.S. Chao, V. A. Stenger, *Talanta* **11** (1964) 271.
- 63 Marathon GTF Technology Ltd., US8815050, 2014, (S.A. Kurukchi, Y. Liu, A. Moodley).
- 64 In [7], P.G.W. Scott, M.L. Parker: “The Analytical Chemistry of Bromine and Its Compounds,” pp. 739–801.
- 65 D.A. Skogg, D.M. West: *Fundamentals of Analytical Chemistry*, 4th ed., Saunders College Publishers, New York 1982, pp. 386–389.
- 66 J.J. Custer, S. Natelson, *Anal. Chem.* **21** (August, 1949) no. 8, 1005–1009.
- 67 R. Frim, S. Ukeles: “Bromine”, in J.E. Kogel, N.C. Trivedi, J. M. Barker, S.T. Krukowski (eds.): *Industrial Minerals and Rocks*, 7th ed., Society for Mining, Metallurgy, and Exploration (SME), 2006, pp. 285–294.
- 68 P.F. Riegler, N.J. Smith, V.T. Torkelson, *Anal. Chem.* **54** (January, 1982) no. 1, 84–87.
- 69 W. Schoniger, *Mikrochim Acta* **123** (1956) no. 155, 869.
- 70 W. Schoniger, “Analytical Procedures for the Flask Combustion Method”, Proceedings of the International Symposium on Microchemistry, Pergamon Press, London 1958, pp. 93–95.
- 71 J.A. Ober: “Bromine”, *2012 Minerals Yearbook*, U.S. Geological Survey (USGS), Reston November 2013.
- 72 S. Boldyryev, P.S. Varbanov, *Chemical Engineering Transactions* **39** (2014) 1423.
- 73 P. Guerra, M. Alae, E. Eljarrat, D. Barcelo in E. Eljarrat, D. Barcelo (eds): *Handbook of Environmental Chemistry: Brominated Flame Retardants*, vol. 16, Springer, Berlin/Heidelberg 2011, pp. 1–17.
- 74 H.C.H. Darley, G.R. Gray (eds.): *Composition and Properties of Drilling and Completion Fluids*, 5th ed., Gulf Professional Publishing, Houston 1988.
- 75 Dow Chemical, Well Pack Fluid-14, Form No. 101-221-83, 1983.
- 76 R.D. Bartholomew, Official Proceedings – International Water Conference, vol. 1, 1998, pp. 827–838.
- 77 C. Nalepa, D.I. Shelton, *Chimica Oggi* **21** (2003) no. 12, 43.
- 78 NRDC, Evaluating Mercury Control Technologies for Coal Power Plants, Washington DC, January 2011.
- 79 ICL to Boost Sales by Making Coal-fired Plants Friendlier, ICL Industrial Products, Beersheva, Israel, 2010, press release.
- 80 Albemarle Mercury Control Division, Mercury Control for Cleaner Energy, Baton Rouge 2011.
- 81 J. Glauser: “BROMINE. CEH Marketing Research Report” in *Chemical Economics Handbook*, SRI Consulting, Menlo Park CA 2009.
- 82 J.A. Ober, U.S. Geological Survey, *Mineral Commodity Summaries*, Reston 2014, pp. 34–35.
- 83 Occupational safety and health guideline for bromine, U.S. Department of Health and Human Service, Washington DC 1992

- 84 ACGIH (ed.): *Threshold Limit Values (TLV) for 1989-1990*, ACGIH, Cincinnati, Ohio, 1989.
- 85 Recommendation of Occupational Exposure Limits (2010–2011), *Journal of Occupational Health* **52** (2010) no. 5, 308–324.
- 86 C.L. Comar, F. Bronner: *Mineral Metabolism – An Advanced Treatise*, vol. 2, Academic Press, New York 1964, Part A, pp. 12–14.
- 87 F.A. Patty (ed.): *Patty's Industrial Hygiene and Toxicology*, 3rd ed., vol. **2 B**, J. Wiley & Sons, New York 1981, pp. 2965–2972.
- 88 J.F. Mills in J.D. Johnson (ed.): *Disinfection of Water and Wastewater*, Ann Arbor Science Publishers Inc., Ann Arbor, MI. 1975, Chap. 6, pp. 113–144.
- 89 Bromine Safety Handbook, DSBG. [www.brandweekernisnet.nl/.../safety\\_handbook\\_bromine\\_pdf](http://www.brandweekernisnet.nl/.../safety_handbook_bromine_pdf) (accessed 15 March 2015).
- 90 Bromine Safe Handling Seminar, Ethyl Corporation, Magnolia, Arkansas, October 4–6, 1988.

## Further Reading

- B. Grinbaum, M. Freiberg: “Bromine”, *Kirk Othmer Encyclopedia of Chemical Technology*, 5th ed., vol. 4, John Wiley & Sons, Hoboken, NJ, 2005, pp. 295–318.