


Bromine

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INTRODUCTION

Bromine, a heavy, mobile, reddish-brown liquid with an intensely irritating odor, is the only nonmetallic element that is a liquid at normal room temperatures. Bromine belongs to Group 17 (VIIA)—the halogen group of elements—in the periodic table. It is a diatomic molecule with the chemical formula Br_2 . Its place in the periodic table is between chlorine (a gas) and iodine (a solid). The atomic number of the bromine atom is 35 and its atomic weight is 79.904. Within wide limits, both the liquid and vapor are diatomic (Br_2).

Carl Lowig, a young chemistry student, originally prepared bromine the summer before beginning his first year at the University of Heidelberg. Winter exams and holidays delayed the continuation of his work long enough for another chemist, Antoine Jerome Balard, to publish a paper in 1826 describing the new element that he had discovered in seawater bitterns. Balard was thus credited with the discovery of bromine, and the French Academy of Science named it after the Greek *bromos*, meaning stench.

The first commercial production of bromine in the United States was from salt brines in 1846 at Freeport, Pennsylvania. In Germany, the first commercial production plant began operation in 1865. This German plant used solutions from the Stassfurt potash factories in its bromine production. Contrary to the method used by Balard to obtain bromine—oxidizing the bromide ion with chlorine—the German process was based on oxidation using manganese dioxide with the aid of sulfuric acid.

Bromine, which occurs naturally in seawater and brines, is extracted using a number of processes. Herbert Dow invented the *blowing out* process for use on Midland (Michigan) brines in 1889. A very small plant in Canton, Ohio, and then a second plant only a little bigger than the first used the blowing out process. Brine electrolysis liberated bromine for a certain period, and then was replaced by the use of chlorine to reduce the bromide to bromine.

Bromine has a number of industrial uses including in flame retardants, drilling fluids, agricultural chemicals, and water treatment.

PRODUCTION AND TRADE

World bromine production capacity in 2003 was estimated to be >563,000 t (Lyday 2003). Two countries and three companies maintain most of this production capacity: the United States (Albemarle Corporation and Great Lakes Chemical Corporation) and Israel (Dead Sea Bromine Group). Of the almost 548,000 t of bromine produced in 2002, the United States accounted for approximately

39% of this amount and Israel accounted for 38%. The three companies also accounted for the majority of the world trade in bromine derivatives.

Principal Producing Countries

China

Official figures indicate that China produces an estimated 40,000 tpy of bromine. This is believed to be a conservative estimate: the Ocean Chemicals Group (OCG) is reported to have a production capacity of 50,000 tpy at facilities north of Laizhou Bay.

Commonwealth of Independent States (CIS)

The U.S. Geological Survey (USGS) estimates that Azerbaijan produced about 2,000 t of bromine in 2002; Ukraine produced about 3,000 tpy; and Russia produced about 3,000 tpy. Kazakhstan and Turkmenistan apparently hold considerable promise for future production based on brines associated with massive natural gas reserves.

France

Overall production estimated for France in 2001 and 2002 was 2,000 tpy. This production rate has been constant since 1996. Elf Atochem SA produces this amount of bromine in southeastern France in its Port-de-Bouc plant, which has a capacity of 12,000 t. The company is investing about \$12.8 million in a specialty brominated derivatives plant based on the bromine from the Port-de-Bouc plant. The derivatives production is destined for the pharmaceutical industry. Albemarle Corporation operates a flame retardant plant at Port-de-Bouc in addition to a bromine derivatives plant at Thann.

India

Although no detailed production figures were found for India, the little information available indicated production levels of about 1,500 tpy, produced from salt production bitterns. Solaris Chemtech Ltd. (formerly BILT Chemicals, Gujarat) is planning to expand yearly production to 10,000 t in the near future.

Israel

Dead Sea Bromine Group (DSBG) produces bromine and bromine derivatives for applications in air conditioning, batteries, cleaning solvents, flame retardants, mineral separation, oil-well drilling, photography, and water treatment. From 1998 through 2002, more

Table 1. DSBG production, 1998–2002, kt

Bromine	1998	1999	2000	2001*	2002*
Elemental	185,200	181,000†	210,000	206,000	206,000
Compounds*	247,000	247,000†	250,000	250,000	250,000

* Estimated numbers.

† Revised numbers.

than 90% of its sales were from exports. Table 1 shows production figures for DSBG during that time period (Yager 2002).

Japan

The Tosoh Corporation, Japan's largest bromine producer, extracts bromine from seawater. It has a reported production capacity of 24,000 tpy (Davenport 2003).

Jordan

The bromine production capacity of the recently constructed Jordan Bromine Company plant at Safi is 50,000 tpy. The plant also produces 35,000 t of calcium bromide and 50,000 t of tetrabromobisphenol for Asian and European markets.

United Kingdom

Until the end of 2003, when the Great Lakes Chemical Corporation closed its plant at Amlwch, Wales, about 28,000 tpy of bromine was extracted from seawater in the United Kingdom.

United States

Current U.S. production of bromine is from inland brines, which are in plentiful supply. The most concentrated domestic brines (up to 5,000 ppm bromide) are in Arkansas and less-concentrated brines (about 2,500 ppm bromide) are in Michigan. An advantage of the Arkansas brines is that they come to the surface at approximately 96°C, a temperature favorable for bromine extraction.

According to USGS data, the quantity of bromine sold or used in the United States from three companies operating in Arkansas and Michigan was equal to production and had a value of \$155 million in 2002. In 2003, the estimated U.S. bromine production was 216,000 t; in 2002 production was 222,000 t (Lyday 2004).

The apparent consumption of bromine in the United States during 2002 was 216,000 t, an increase from 214,000 t in 2001 (Lyday 2004). The estimated bromine consumption for 2003 was 211,000 t. U.S. bromine usage is divided into the following categories and percentages: fire retardants (40%); drilling fluids (24%); brominated pesticides (12%); biocides/water treatment chemicals (7%); and other products (17%). The other products are photographic chemicals, rubber additives, dyes, pharmaceuticals, brominated intermediates (used to manufacture products and bromide solutions used alone or in combination), and gasoline additives. The brominated gasoline additives and halon markets have virtually disappeared because of environmental considerations and legislation. Unofficial sources predict that other markets will show either modest growth or decline in the coming years, except for water treatment applications, which should demonstrate good growth.

Overall, demand for bromine in the United States was estimated to grow at a modest yearly rate of about 1% to 2% from 2001 through 2006. This estimate was based on the assumption that no new, major legislative restrictions would be placed on bromine chemical use during that period.

The USGS maintains bromine production data. The apparent consumption of elemental bromine in the United States has been defined as production plus imports minus exports. Table 2 gives the

Table 2. U.S. supply and demand data for elemental bromine, 1995–2004, kt*

Year	Annual Capacity	Production	Imports	Exports	Apparent Consumption
1995	259	218	2.22	3.22	206
1996	290	227	0.42	2.92	225
1997	337	247	1.65	2.33	249
1998	337	230	1.19	1.49	235
1999	337	239	1.97	2.11	239
2000	349	228	5.47	1.87	238
2001	715	212	5.61	3.71	214
2002	261	222	2.02	6.07	216
2003†	262	216	1.92	2.28	210
2004†	No data	222	No data	No data	220

* Data compiled from various USGS sources.

† Data based on preliminary estimates.

Table 3. U.S. imports of bromine chemicals, 1995–2003, kt*

Year	Inorganic Chemicals		Organic Chemicals		Total	
	Gross Weight	Bromine Content	Gross Weight	Bromine Content	Gross Weight	Bromine Content
1995	3.81	2.64	5.85	4.88	9.66	7.52
1996	15.17	11.61	6.52	5.09	21.69	16.70
1997	38.84	6.75	8.91	6.90	47.75	13.65
1998	6.98	5.00	8.99	6.77	15.97	11.77
1999	8.74	6.36	7.40	0.78	16.14	7.14
2000	61.37	13.96	7.76	5.86	69.13	19.82
2001	67.16	11.00	5.95	4.30	73.11	15.30
2002	21.36	4.52	4.92	0.18	26.28	4.70
2003	51.87	7.66	3.28	0.25	55.15	7.91

* Data compiled from various USGS sources.

supply and demand data for elemental bromine from 1995 through 2002, and estimates for 2003 and 2004.

Most bromine trade involves bromine derivatives rather than elemental bromine. The United States imports a wide range of bromine-containing chemicals, including bromide salts such as ammonium bromide, calcium bromide, potassium bromide, and sodium bromide, as well as sodium bromate and potassium bromate. Other imported bromine chemicals were mainly organics, largely brominated fire retardants from Israel. Table 3 lists U.S. imports of bromine chemicals for 1995 through 2003.

Exports of bromine chemicals from the United States to other countries have been estimated to be about 49,000 to 51,000 t (gross weight). The major portion of this quantity was flame retardants, estimated to be about 30,000 t.

Principal Producing Companies

Albemarle Corporation

The Albemarle Corporation, headquartered in Richmond, Virginia, was spun off as a separate company from the Ethyl Corporation in 1994. The company has two operating divisions: the Fine Chemicals Division, which produces performance chemicals, pharmaceuticals, and agricultural products; and the Polymer Chemicals Division, which produces fire retardants (brominated and non-brominated), catalysts, and adhesives. Total annual sales of about

Table 4. World production of bromine, 1995–2003, kt^a

Year	China	France	Israel	Japan	United Kingdom	United States	CIS [†]	Other	Total
1995	32.7	2.3	130	15	26.2	218	5.6	1.8	432
1996	41.4	2.0	160	15	30.6	227	5.1	1.9	483
1997	50.1	2.0	180	20	35.6	247	5.1	1.9	542
1998	40.0	2.0	185	20	30.0	230	5.2	1.9	514
1999	42.0	2.0	181	20	55.0	239	5.2	2.4	547
2000	42.0	2.0	210	20	32.0	228	5.2	2.4	542
2001	40.0	2.0	206	20	35.0	212	5.2	2.4	523
2002	42.0	2.0	206	20	35.0	222	5.2	7.4	540
2003 [‡]	42.0	2.0	206	20	35.0	216	5.2	22.4	549

* Data compiled from various USGS sources.

† CIS here includes Azerbaijan, Turkmenistan, and Ukraine.

‡ Estimated figures.

\$980 million have been reported. Bromine is critical to many of the company's products. Aside from manufacturing brominated fire retardants, Albemarle also produces other products containing bromine, including metal alkyls, inorganic bromides, and a number of fine chemicals. Albemarle's bromine-based operations are in the United States and France. In 1999, Albemarle Holdings (an Albemarle affiliate) established a joint venture with Arab Potash/Jordan Dead Sea Industries to construct a bromine and bromine derivatives complex at Safi, Jordan, on the Dead Sea. Phase one, which opened in October 2002, was a bromine unit and a production facility for inorganic bromides and hydrogen bromide. The second phase involves the construction of a Sayytext CP-2000 (tetrabromobisphenol) flame-retardant plant.

Dead Sea Bromine Group

DSBG, headquartered in Beer Sheva, Israel, is the world's largest producer of elemental bromine. Total annual sales are more than \$500 million (Y. Gramse, personal communication). The company's elemental bromine plant is on the shore of the Dead Sea, and an affiliated company, Dead Sea Works (a producer of potash and other inorganic chemicals), supplies the raw material for its bromine production. Israel Chemicals, which has its headquarters in Tel Aviv, owns both companies. DSBG—through subsidiaries such as Bromine Compounds (Ramat Hovav, Israel)—produces a broad range of organic and inorganic bromine compounds.

In addition to elemental bromine and bromine derivatives in Israel, DSBG also produces bromine derivatives in the Netherlands at its Eurobrom facility. DSBG and its subsidiaries are grouped into eight business units that produce elemental bromine, flame retardants, biocides, agrochemicals, oil-field chemicals, industrial chemicals, organic intermediates, and fine chemicals.

In 2003, DSBG and Manac of Japan signed an agreement for long-term cooperation to produce and market a flame retardant for engineering plastics. Also in 2003, DSBG entered into a long-term strategic sourcing agreement for elemental bromine and certain bromine derivatives with the Great Lakes Chemical Corporation.

Great Lakes Chemical Corporation

Great Lakes Chemical Corporation (GLCC), with headquarters in Indianapolis, Indiana, has total yearly sales of more than \$1.5 billion. It has four operating units: water treatment, polymer additives, performance chemicals, and energy services and products. All these units generate bromine-containing products. The polymer additives unit produces flame retardants and polymer stabilizers. The flame retardant segment uses brominated and nonbrominated compounds.

The performance chemicals unit uses elemental bromine, methyl bromide, and other bromine products. GLCC's elemental bromine production is primarily from brines in Arkansas, but it also operates a plant in the United Kingdom (Associated Octel) that extracts bromine from seawater.

Brominated compound production, especially flame retardants, is focused in the United States, but there is also production in the United Kingdom. GLCC has formed a joint venture for tetrabromobisphenol with DSBG at Ramat Hovav, Israel. In 2003, GLCC and the ICL Industrial Products Division (Israel) announced a global agreement whereby the latter would supply bromine and bromine compounds to GLCC.

World Production Statistics

In 2002, the United States continued to maintain its leading position in bromine production, which was estimated at about 222,000 t that year. Israel was second with 206,000 t. These two countries accounted for about 78% of the world's elemental bromine production of 550,000 tpy. Other leading producers accounted for the remaining 22%, including China, France, India, Japan, the United Kingdom, and CIS members.

Table 4 gives production data for the world's largest producers of bromine for 1995–2003. Harben (2003) presented slightly different figures that reflect data not available through USGS.

OCCURRENCE

Distribution in Nature

Bromine is distributed widely in nature as bromide salts and as organobromine compounds, which are produced by various marine organisms. Bromine is present in the hydrosphere, mainly as soluble bromide salts in seawater, salt lakes, inland seas, natural brine wells, and in evaporite chloride minerals. Concentrations vary from 65 mg/L in seawater up to 6.5 g/L in the southern basin of the Dead Sea. Its abundance in igneous rocks is 0.00016% by weight, whereas seawater has an abundance of 0.0065% by weight.

The only minerals that contain bromine are some silver halide ores: bromyrite (AgBr), embolite [Ag(Cl, Br)], and iodobromite [Ag(Cl, Br, I)]. H.E. Boeke (1908) determined the distribution of bromine in marine evaporite minerals, and in the solutions from which they crystallize.

Terrestrial plants contain an average of about 7 ppm bromine. The highest bromine content in animal life is found in marine animals (e.g., fish, sponges) and crustaceans. Animal tissues contain 1 to 9 ppm bromide whereas animal blood has a content of 5 to 15 ppm bromine.

Table 5. World bromine reserves, 2005 estimate, kt

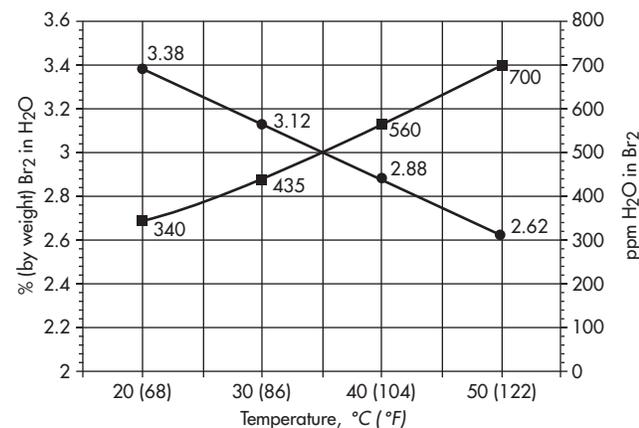
Country	Reserves	Country	Reserves
Azerbaijan	300	Japan	Unlimited*
China	Unlimited*	Spain	1,400
France	1,600	Turkmenistan	700
India	Unlimited*	Ukraine	400
Israel/Jordan	1,000,000	United Kingdom	Unlimited*
Italy	Unlimited*	United States	11,000

Adapted from Lyday 2005.

* Available from waste bitterns associated with solar salt.

Table 6. Physical properties of bromine

Property	Value
Freezing point	-7.25°C
Boiling point	58.8°C
Density of liquid	
(20°C)	3.1226 g/mL
(25°C)	3.1055 g/mL
(30°C)	3.0879 g/mL
Density of vapor, 0°C, 101.3 kPa	7.139 g/L
Refractive index, 20°C	1.6083
Heat of fusion, -7.25°C	66.11 J/g
Heat of vaporization, 50°C	187 J/g



Adapted from Great Lakes Chemical Corporation, undated.

Figure 1. Mutual solubility of bromine and water

Commercial Sources and Reserves

The Dead Sea is today the richest commercial source of bromine; its brines contain 5 g/L bromine in the open sea, 6.5 g/L in the southern basin (near Ein Bokek, Israel), and up to 12 g/L in the end brine from potash production. This end brine serves as an almost unlimited source of raw material for Israeli and Jordanian bromine production. Other important bromine sources are underground brines in Arkansas (3 to 5 g/L) and Michigan (2 to 3 g/L) (United States), Russia, China, and the United Kingdom; bitterns from mined potash (France and Germany); and seawater or seawater bitterns in France, India, Italy, Japan, and Spain.

Table 5 gives a breakdown of estimated world bromine reserves by country (Lyday 2005). The Dead Sea is estimated to contain about 1 billion t of bromine. The bromine content of underground brines in Poland has been estimated at 36 Mt.

Analytical Methods for Bromine and Bromides

The analysis for liquid bromine and bromine is based on its reaction with an aqueous potassium iodide solution to form molecular iodine, followed by its titration with a standard sodium thiosulfate solution. Bromine vapor can also be determined by absorption into aqueous potassium iodide solution and subsequent iodometric titration of the liberated iodine. Impurities in bromine (e.g., chloride, iodide, sulfur, water, organic compounds, and heavy metals) can be determined quantitatively.

Other methods for determining bromine are the Mohr, Volhard, and Fajans methods, silver nitrate titration using a silver indicator electrode, and a gravimetric method (silver bromide). Some methods used for determining trace amounts of bromide quantitatively are

- the van der Meulen method, which is useful in the presence of large chloride concentrations;
- constant-current and constant-potential coulometry, which can determine fractions of a milligram to several grams of bromide;
- ion chromatography;
- polarography for microgram quantities; and
- a spectrophotometric method, which is useful for microgram quantities in the presence of chloride.

Bromine in organic compounds can be determined by chemical methods following their oxidation and the reduction of bromine to bromides. The bromine content in the organic compounds can be determined subsequently by one of the following methods: neutron activation, x-ray fluorescence (XRF), infrared spectroscopy, or atomic emission spectroscopy.

PROPERTIES OF BROMINE

Physical Properties

Bromine liquid volatilizes readily at room temperature into reddish vapor, which is highly corrosive to many materials and human tissues. The liquid and vapor are diatomic (Br₂) up to about 600°C. Table 6 gives some of bromine's most important physical properties (Grinbaum and Freiberg 2002).

Bromine is fairly soluble in water, having the following solubilities at the corresponding temperatures: 3.41 g/100 g solution at 20°C; 3.35 g/100 g solution at 25°C; and 3.33 g/100 g solution at 40°C. The solubility of bromine increases in the presence of bromide or chloride ions from complex ion formation (e.g., formation of tribromides and pentabromides). Bromine is also soluble in nonpolar solvents (e.g., carbon tetrachloride, chloroform, carbon disulfide, and ether) and polar solvents such as methyl alcohol and sulfuric acid. Figure 1 shows the mutual miscibility of bromine and water.

Chemical Properties

Bromine, as other halogens, has a tendency to accept an electron to form either a negative bromide ion (Br⁻) or a single covalent bond (-Br). Except for helium and neon, the other elements of the periodic table are able to form halides with the halogens, including bromine. The bromides that are primarily ionic in nature tend to have high conductivities in the fused state and high boiling points, and are not susceptible to hydrolysis if they are soluble bromides. The predominantly covalent bromides that can form are volatile and nonconductive in the liquid state, and usually undergo hydrolysis. The nonmetallic bromides generally hydrolyze to hydrogen bromide and an oxy-acid containing the other element.

Reactions with Hydrogen and Metals

Bromine reacts with hydrogen at elevated temperatures to form hydrogen bromide. Heated charcoal and finely divided platinum

metal are used as catalysts for this reaction, which is the basis for the commercial production of hydrogen bromide. Bromine reacts with all metals except tantalum and niobium; elevated temperatures are sometimes necessary to accomplish this conversion. The reaction of bromine with lead, magnesium, nickel, and silver forms a surface coat of bromide that resists further attack. This protective coating permits the use of lead and silver as linings in bromine containers. Metals corrode more rapidly from bromine in the presence of moisture than in its absence, probably because of the formation of hydrobromic acid (HBr) and hypobromous acid (HOBr).

Reactions in Water

When bromine dissolves in water, it undergoes partial disproportionation to form hypobromous acid, hydrogen ions, and bromide ions. The hypobromous acid is relatively stable only in solution and decomposes under the influence of heat, light, or copper catalysis to produce HBr and oxygen. In the dark, hypobromous acid decomposes to bromic acid (HBrO₃) and bromine. Bromic acid is relatively unstable and slowly decomposes to form bromine and oxygen (Grinbaum and Freiberg 2002).

In basic solution, bromine reacts rapidly to form bromide (Br⁻) and hypobromite (OBr⁻) ions. It is necessary to maintain this reaction below 0°C to limit the disproportionation of hypobromite to bromate and bromide.

Reactions with Organic Compounds

Bromine can react with organic compounds in various ways (Ioffe and Kampf 2001). Typical of such reactions are the addition of bromine to unsaturated hydrocarbons and the substitution of hydrogen on an organic substrate, with corresponding release of hydrogen bromide. It is possible to carry out reactions both in the liquid or vapor phases and in the presence or absence of solvents or catalysts. Some of the solvents used are chloroform, carbon tetrachloride, acetic acid, and hydrobromic acid. Lewis acid catalysts (e.g., aluminum chloride) are used frequently for the bromination of aromatic compounds, whereas light or peroxide catalysts are used in the bromination of aliphatic compounds.

The indirect reaction of other functional groups with bromine derivatives is the preferred method for the preparation of some organic compounds. An example is the preparation of methyl bromide (an alkyl bromide), which is best prepared by the reaction between methanol and hydrogen bromide. An alternate preparation of alkyl bromides is by the reaction of hydrobromic acid to an olefinic compound.

TECHNOLOGY

Processing Methods

Current methods for bromine production use chlorine to oxidize bromide to bromine. The principal processing steps follow:

1. Oxidize bromide to bromine.
2. Strip bromine from the aqueous solution.
3. Separate the bromine from the resulting vapor.
4. Purify the bromine.

Differences between various processes generally are manifested in the stripping and purification steps.

The two principal processing variations are the *steaming-out process* and the *blowing-out process*.

Steaming-Out Process

The current process used for producing bromine from bromide-containing brines (1 to 5 g/L Br⁻) is based on the *hot* or *steaming-out process* first described by Konrad Kubierschky in 1906 (Jolles

1966). It consists of simultaneous chlorination and steam blowing. The brine is preheated, usually to 75°–80°C, before its introduction into the Kubierschky tower, and then heated inside the tower by live steam to near boiling. The bromine is steam-distilled as it is being set free by the chlorine. The distillation steam is a small fraction of the live steam supplied to heat the brine. The steaming-out process requires heating the brine to near boiling and reducing the partial pressure of bromine (and chlorobromide) in the effluent brine to nearly zero to improve the stripping of the bromine from the brine. Drying the brine usually is achieved with sulfuric acid.

The advantage in the steaming-out process is that bromine is condensed directly from the steam, as opposed to the air blowing-out process, in which the bromine is trapped in an alkaline or reducing solution to concentrate it.

Blowing-Out Process

The blowing-out process uses air rather than steam. (The cost of steam to heat ocean water, with its very low bromine content of 65 mg/L, is prohibitively expensive.) In this process, bromide-containing water is pumped to the top of blowing-out towers. Sulfuric acid and chlorine are added above the pumps to ensure that mixing occurs in the brine during its ascent. An excess of about 15% chlorine is used over the theoretical amount required. Air is drawn through the towers, thus sweeping out a mixture of bromine and chlorine (or bromine chloride) from the descending water. The bromine-laden air is drawn next through the absorber towers in which it is scrubbed countercurrently with a sodium carbonate solution. To remove the 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 transferred to a storage tank and then to a reactor where it is treated with sulfuric acid and steamed to release bromine. Subsequently, the bromine is condensed.

Production from Wastes

An increasing amount of bromine is being produced from wastes. Hydrogen bromide, which is emitted as a by-product in many organic reactions, is a major source for this kind of bromine production. Part of the hydrogen bromide comes from incinerating organic wastes in a bromine recovery unit (BRU). The emitted flue gases from the BRU contain hydrogen bromide and molecular bromine, which are usually separated before the hydrogen bromide processing. The process used to recover bromine is similar to that used for producing bromine from bromides, that is, by oxidation with chlorine gas or another oxidant.

Another approach tested recently is recovering bromine from hydrogen bromide waste streams using electrolytic membranes to decompose the hydrogen and bromine. This process apparently has not yet been commercialized.

Product Specifications

Table 7 lists the American Chemical Society (ACS) specifications for reagent grade bromine and typical product specifications for purified bromine. The bromine content (by weight %) represents a minimum value, whereas the water and chlorine contents are maximum values (Grinbaum and Freiberg 2002).

MARKETS

Uses of Bromine

The synthesis of a wide range of brominated organic compounds involves the direct or indirect consumption of bromine. For the majority of brominated flame retardants (BFRs), bromine reacts with a suitable starting material to form the flame retardant (FR) along with one molecule of hydrobromic acid for each atom of

Table 7. Specifications for elemental bromine

Parameter	ACS Specification	Product Specification
Bromine content, %	99.5	99.9
Specific gravity, 20/15°C	na [*]	3.1
Water, ppm	na	30
Chlorine, ppm	500	100
Organic halogen compounds, ppm	Must pass ACS test	80
Nonvolatile matter, ppm	50	30
Iodine, ppm	10	Must pass ACS test
Sulfur (as S), ppm	10	Must pass ACS test
Heavy metals (as Pb), ppm	2	Must pass ACS test
Nickel, ppm	5	Must pass ACS test

* na = not available.

bromine contained in the end product. The hydrobromic acid produced is further reacted (e.g., with an alcohol to form an alkyl bromide) or neutralized to form a bromide salt.

Before describing uses, a few words should be devoted to the use of bromine in ethylene dibromide (EDB) as a gasoline additive. Bromine demand for this use steadily declined each year after the U.S. Environmental Protection Agency (EPA) issued regulations in the 1970s to reduce and eliminate lead in gasolines. (The EDB acts as a lead scavenger by converting lead oxides to lead bromide, which then escapes along with the engine exhaust.) An EPA mandate to eliminate all the lead from motor vehicle gasoline formulation by 1996, therefore, decreased EDB consumption drastically. Some lead is still used in aviation fuel formulations, although most of the small amount of U.S. production is exported to countries still having less-strict environmental legislation.

Flame Retardants

BFRs are still a growing market. The total global FR market has an estimated annual volume of approximately 2.0 billion lb (about 909,000 t), valued at about \$2.2 billion. Halogenated materials, which include halogenated phosphorous FRs, make up about 35% to 40% of this volume and are 55% by value. BFRs alone account for 25% of the volume and 35% of the value (Tullo 2003). Brominated polymers are used in FR applications and bromine-containing epoxy sealants are used as FRs in semiconductor devices.

The BFRs (which are typically brominated aromatic or cyclic aliphatic compounds), can be the additive type, where the FRs are incorporated as a constituent in mixtures with polymers before, during, or more likely after polymerization; or the reactive type, where the FR is bonded chemically to the polymer itself. The BFR slows down or stops flame generation in polymer systems by interfering with the chain reaction mechanism of combustion, that is, by extinguishing radicals that serve to propagate oxidation. Synergists such as antimony trioxide, antimony pentoxide, or zinc borate add to the effectiveness of BFRs as do halogens when they are present in the polymer.

The consumption of bromine in FRs has risen steadily over the last several decades, mostly because of increased use of electronics and communications products. Because of the significant economic downturn in 2001, however, consumption fell drastically to its lowest level in many years.

Drilling Fluids

The oil and gas drilling industry uses calcium, zinc, and sodium bromides to prepare high-density, clear drilling, completion, packer,

and workover fluids (Ukeles and Freiberg 2002). These brine fluids are used in deep, high-pressure oil and gas wells; they do not plug the formation in workover and completion operations, as conventional drilling muds can do. Such bromide salt brine usage has led to higher production rates and longer production lifetimes. For such applications, calcium bromide is the largest volume bromide salt in use, followed closely by zinc bromide and sodium bromide. Sodium bromide finds use in specialized situations where calcium or zinc brines could cause a minimal amount of swelling, or in carbon dioxide-containing strata where there is a danger of calcium carbonate precipitation.

The bromine-based completion fluids are used in both offshore and onshore drilling operations. Recent expansion in drilling activity and in the type of activity—namely deep, high-pressure wells—has contributed to the rapid growth of this market.

The inorganic bromides used in this application are prepared by neutralizing hydrobromic acid, which represents one of the two largest uses for this acid.

Brominated Agricultural Chemicals

Methyl bromide is currently the major bromine-containing pesticide used worldwide, but its use is declining. It is a broad-spectrum pesticide used to control pest insects, nematodes, weeds, pathogens, and rodents. About 25,000 t of methyl bromide were produced in the United States in 1999 for both domestic and foreign markets; much of it was produced as a by-product of BFR manufacture. Applications include soil fumigation, commodity and quarantine treatment, and structural fumigation. Global production in 1999 was estimated to be about 52,000 t.

When used as a soil fumigant, methyl bromide usually is injected into the soil at a depth of 30 to 60 cm before a crop is planted. This effectively sterilizes the soil, killing most soil organisms. After injection, the soil is covered with a tarp for 24 to 72 hr to slow the movement of methyl bromide from the soil to the atmosphere.

The three major manufacturers of methyl bromide—Albemarle Corp., GLCC, and Israel's DSBG—account for 75% of global production.

Biocides/Water Treatment

Even with continued dominance of chlorine in most of the water treatment sector, brominated compounds continue to make inroads into that market. This is probably due in part to environmental restrictions that chlorine has experienced in recent years. Among the advantages that bromine enjoys over chlorine in some water treatment areas are the following:

- Brominated compounds are less likely to form undesirable, halogenated organic compounds.
- Bromine has been found to be more efficient at higher temperatures than unstabilized chlorine.
- Brominated compounds are more effective at lower concentrations and at a higher pH than chlorine, thus allowing for greater throughput in waste treatment plants and cooling towers.
- Debromination of treated effluent streams is unnecessary, and any bromamines that are formed degrade more rapidly than the corresponding chloramines.
- Brominated products are estimated to be three times more effective than chlorine at controlling algae in cooling towers.

Bromine (e.g., bromochlorodimethylhydantoin [BCDMH]) has also made gains in the consumer water conditioning market as a

biocide for spas, pools, and hot tubs. The brominated hydantoin releases both hypochlorous and hypobromous acid in solution, where the latter is more effective at higher pH.

Brominated Intermediate

Brominated compounds are frequently used as intermediates in the production of other organic chemicals such as agrochemicals, pharmaceuticals, and dyes. For such applications, no bromine is present in the end product. Some of the bromine released during production processes that use these intermediates may be recovered and recycled (generally as hydrobromic acid or as a bromide salt); there are losses, however, that result when the by-product becomes too dilute or too contaminated. Some examples of chemicals that are used as intermediates are bromoacetyl bromide (cefotetan, labetalol), n-hexyl bromide (a building block for fragrances and dyes), 4-bromoaniline (metobromoron, resorantel), and 2-bromopropionic acid (naproxene, prilocaine).

Other Uses

A number of pharmaceuticals are prepared in the form of bromides or hydrobromides. One example is the antitussive (alleviates or prevents coughs) dextromethorphan hydrobromide. Bromide salts also find use in some rechargeable batteries.

More than 5,000 t of bromine are used in the United States in the production of bromobutyl rubber for the inner linings of automobile tires. The majority of tire manufacturers prefer the improved performance of the bromine derivative over the chlorine-containing compound (i.e., chlorobutyl rubber).

Bromine is capable of desulfurizing fine coal (Grinbaum and Freiberg 2002). Bromine and its salts are known to recover gold and other precious metals from their ores by serving as an oxidant and complexant of gold.

Zinc-bromine storage batteries are being developed as load-leveling devices for use in electric utilities. In addition, photovoltaic batteries have been made from selenium or boron doped with bromine. Bromine also is used in quartz-halide light bulbs.

Product Pricing

Data from USGS indicated that the average price of purified elemental bromine was 99 cents/kg (44 cents/lb) during 2002. This was an increase from 67 cents/kg (30 cents/lb) for 2001. The price cited for 2001 represents a sharp decrease from the 2000 price, which was listed as 90 cents/kg (41 cents/lb) (Davenport 2003). According to Lyday (2005), prices peaked again in 2002 at 99.2 cents/kg (45.1 cents/kg) before declining to 72.0 and 70.0 cents/kg (32.7 and 31.8 cents/lb) in 2003 and 2004, respectively.

Packaging

Bromine is generally supplied as a liquid in drums or portable tanks (isotanks), depending on the quantities required by the customer. Hazardous Materials Regulations (HMR) are based on the recommendations of the United Nations Economic Commission for Europe (UNECE; 2005). Known as the "Orange Book," the UNECE directory provides an extensive list of dangerous goods and their control in transport by air, rail, road, sea, and inland waterways. It covers classifications and definitions of all dangerous substances; packaging, labeling and relevant shipping documentation; and training of transport workers.

In the United States, bulk quantities of bromine are shipped in lead-lined pressure tank cars or nickel-clad pressure tank trailers (filled to 92% of capacity). International shipments made by DSBG are in 15.2 to 23.3 t (5,300 to 8,000 L) lead-lined tank containers (isotanks). For smaller quantities of bromine, lead-lined

tanks ("goslars") of 3.5 t (4 t packed on one isoframe) and 400-kg (140-L) drums are used. Packaging is designed according to UN recommendations for Packing Group I.

Problems may be encountered in shipping and storage because of the relatively high freezing point of bromine (i.e., -7.25°C). If bromine freezes in a tank car, warm water—below 54°C —must be circulated through the car's heating coils.

Engineering Materials

Because bromine is highly hygroscopic, improper handling may cause its water content to increase to >300 ppm. When water content and organic matter content of bromine increase, the probability that it will corrode engineering materials increases. Therefore, bromine must be stored under dry nitrogen or dry air. Bromine with <30 ppm water content is noncorrosive to many nonferrous metals, including lead, nickel, tantalum, Hastelloy B, Hastelloy C, and Monel.

Some of the points previously mentioned are amplified below:

- Lead and lead-lined steel are commonly used in process equipment and storage containers when bromine is dry. The protective layer of lead bromide formed on the interior of a storage vessel allows it to be used with bromine with a water content up to 75 ppm.
- Glass has excellent resistance to wet or dry bromine corrosion.
- Nickel and nickel alloys such as Monel 400 and Hastelloys B and C are corrosion resistant to dry bromine (<30 ppm water) but are attacked rapidly by wet bromine.
- Tantalum and niobium both have excellent resistance to corrosion to either wet or dry bromine and can be used at temperatures up to 149°C .
- Steel and stainless steel are not recommended as construction materials because of corrosive bromine and bromine vapors.
- Fluorinated plastics such as Kynar, Kalrez, Halar, and Teflon (polyvinylidene fluoride [PVDF], perfluoroelastomer parts, ethylene-chlorotrifluoro-ethylene [ECTFE], and polytetrafluoroethylene [PTFE], respectively) are resistant to bromine corrosion and are used in valves, piping, gaskets, and linings.
- It is not recommended to use other types of polymers if contact with bromine is imminent.

Storage

Bromine for laboratory or pilot use generally is purchased in glass bottles. It is poured or pumped into small glass, ceramic, or lead-lined vessels that are equipped with PTFE stopcocks. The bottles are stored in their cartons in a dry, cool location away from direct sunlight. The storage temperature should not fall below the freezing point of bromine, -7°C .

Drum, tank truck, or carload quantities of bromine are stored in lead, lead-lined steel, or glass-lined steel storage tanks, which feed into a particular process or reaction. When using larger storage tanks (where bottom outlets cannot be used), the bromine should be pumped out of the tank with nickel, PVDF, or PTFE pumps.

Drums should be stored empty or full in an upright position, in a cool (above -7°C), dry place. Exposure to heat will cause a dangerous pressure buildup to develop. Protection from moisture and humidity is extremely important. GLCC offers bromine in non-returnable 120-gal steel cylinders that hold about 2,800 lb of bromine. The precautions previously outlined for drum storage also apply to cylinders.

Storage tanks also should be protected from moisture or humid air, because bromine will absorb moisture. When bromine is exposed to air having a normal summer dewpoint of 5° to 10°C , it

will equilibrate with about 70 to 80 ppm water. Wet bromine can severely corrode many metals. A slight positive pressure (0.1 in. of water) should be maintained in storage tanks by purging with dry air or dry nitrogen.

Transport of Bromine

A number of options are available for the transport of bromine. For example, GLCC ships bromine in bulk, using lead-lined, double-barrel tank trailers with a capacity of about 600 gal. Another option offered by GLCC is bromine in bulk either in 2,400 gal (56,000 lb) or in 4,400 gal (110,000 lb) lead-lined tank cars. The liquid bromine supply configurations used by DSBG (e.g., drums, goslars, or isotanks) were previously described.

Because bromine is a very corrosive and toxic material, regulations mandate which materials can be placed in proximity with, or require separation from, bromine. These regulations are available in the International Maritime Dangerous Goods (IMDG) code that covers regulations for international shipping.

U.S. Department of Transportation (DOT) regulations allow the transport of bromine within the United States, although it must be packaged, marked, labeled, placarded, stowed, segregated, and certified in accordance with the IMDG code, provided that part or all transportation is by vessel (Gilmour 1998). The total quantity in one tank may not be less than 88%, or more than 92% of the tank volume.

HEALTH AND SAFETY FACTORS

Effects of Exposure

Bromine has a sharp, penetrating odor. Bromine exposure—by liquid contact or vapor inhalation—is a considerable hazard with potential risk for serious injury and even death (Reineke 1978). The liquid rapidly attacks skin and other tissue to produce irritation and necrosis. Vapor concentrations of about 1 ppm are unpleasant, can cause eyes to water, and are highly irritating to the entire respiratory tract; 10 ppm becomes intolerable, even for more than a few moments.

If 10 ppm or more of toxic bromine are inhaled, severe burns and serious inflammation in the respiratory tract result, and these are frequently followed by pneumonia (Grinbaum and Freiberg 2002). Some symptoms of overexposure include coughing, nose-bleed, feeling of oppression, dizziness, headache, and possibly delayed abdominal pain and diarrhea.

Skin contact with liquid bromine produces an initial mild cooling sensation, followed by a heating sensation. If bromine is not removed by washing the area affected with water, the skin will turn red, then brown, and the resulting deep burn is slow to heal. Contact with concentrated bromine also results in burns and blisters. Small areas in the laboratory that have become contaminated with bromine can be neutralized with a 10% solution of sodium thiosulfate. Such a solution should be kept readily available when working with bromine.

Vapor concentrations of 500 to 1,000 ppm by volume are dangerous to life at exposures for 0.5 to 1.0 hr. With respect to respiratory exposure, the Occupational Safety & Health Administration (OSHA) threshold limit value–time weighted average is 0.1 ppm in air for an 8-hr working day and 40-hr workweek. Monitoring devices are available for determining bromine concentrations in air.

Protective Equipment for Bromine Handling

Processes incorporating bromine should use totally enclosed systems. The minimum safety equipment requirements for handling bromine in the laboratory are chemical goggles, rubber gloves

(Buna-N or neoprene rubber), laboratory coat, and fume hood. For handling bromine in a manufacturing plant, personal protective equipment should include hard hat, goggles, neoprene full-coverage slicker, Buna-N or neoprene rubber gloves, and neoprene boots. When evacuating from an area where a release of bromine has occurred, a full-face respirator with an organic vapor–acid gas canister is desirable.

Fire Precautions

In case of fire, personnel should wear a self-contained breathing apparatus when working in an area containing bromine compounds. Bromine does not burn, but it is a strong oxidizer and reacts violently with aluminum, titanium, sodium, and potassium. Wood, paper products, fabric, petroleum products, plastics, and other organics may combust spontaneously in the presence of liquid bromine.

REGULATORY AND ENVIRONMENTAL CONSIDERATIONS

Methyl Bromide

Methyl bromide, which is a known toxic substance to human beings that damages the central nervous and respiratory systems, also may contribute significantly to the destruction of the Earth's stratospheric ozone layer. In September 1997, at the Ninth Meeting of the Parties to the Montreal Protocol, participating members agreed to a schedule for the reduction in the use of this fumigant. In developed countries, most uses were slated to cease in 2005 except for certain exemptions, and developing countries would have until 2015 to phase out methyl bromide.

Methyl bromide was listed as a Class I ozone-depleting substance in the 1990 Clean Air Act Amendments in the United States, which previously had instituted a ban that would take effect in 2001. The U.S. Congress extended the phaseout of methyl bromide to coincide with the 2005 ban set by the Montreal Protocol. To avoid any trade differences that might arise between U.S. growers and those in countries that still would have access to methyl bromide after 2005, the EPA has stated that in the absence of alternatives for methyl bromide, it would support limited, essential uses of this material.

Recently, a UN body (the Technology and Economic Assessment Panel) approved a U.S. request for exemptions from a ban on methyl bromide. This panel recommended exemptions for methyl bromide on U.S. crops such as strawberries, raspberries, eggplant, and tree seedlings. These exemptions have been the focus of objections from the Natural Resources Defense Council.

Flame Retardants

The polybrominated diphenyl ethers (PBDEs) are the BFRs that have been under the most scrutiny because of their apparent persistence in the environment and concerns for bioaccumulation. Recently, GLCC announced a voluntary U.S. phaseout of two PBDEs. The two flame retardants—pentabromodiphenyl ether (penta-BDE) and octabromodiphenyl ether (octa-BDE)—were phased out by the end of 2004 (Hogue 2003). (The phaseout of these two PBDEs is not considered to be as critical as would be any exit from deca-BDE [a styrenics additive], which is produced in the highest volume of the PBDEs.)

Because of environmental regulations, many polymer fabricators are now trying to avoid BFRs altogether. BFR suppliers themselves are diversifying their product offerings to include nonbrominated FRs. Thus, although both Albemarle's and Great Lakes' flame-retardant businesses were 100% bromine-based less than a decade ago, the situation has changed significantly. Through acquisitions and internal developments, roughly 35% of their sales now come from nonbrominated FRs.

OUTLOOK AND FUTURE TRENDS

Unofficial growth estimates for the bromine industry have been placed at about 2% per year throughout 2008. Bromine production from seawater is becoming an expensive process and will eventually become infeasible. No new areas of growth are expected in the near future, so the majority of bromine will continue to be consumed by FRs, intermediates, oil drilling, and biocide applications. The bromine industry has a negative image, which it feels is unjustified. The results from upcoming risk assessments of BFRs (e.g., tetrabromobisphenol A [TBBA], deca-BDE, penta-BDE, and hexabromocyclododecane [HBCD]) will be crucial to the future of the industry. Lobbying activities and industry panels will play an important part in the future of the bromine industry.

The price of elemental bromine and the prices of bromine compounds and derivatives are correlated. The current lower prices of the major brominated products, along with regulatory pressures, threaten the industry's reinvestment capabilities in new R&D and production facilities and thus its long-term viability. In addition, the geographical shift of major industrial chemical activities from the West to China will continue to influence this industry along with others.

China

Approximately 80% of Chinese bromine is produced from saturated brines in Shandong Province (Bohai Bay). The remaining 20% is produced from seawater. Bromine reserves in Shandong are estimated to be 1.0 to 1.5 Mt. Many of the big Chinese producers are also in the process of going downstream to produce brominated compounds, and their relocation to bromine resources is being observed. Also of note is the trend of consolidating smaller bromine plants into one large company. The Chinese bromine industry has the ability to produce new products and improve the quality of existing products (e.g., FRs, dyestuffs, pharmaceuticals, and bromides) rapidly. Many of the bromine industry customers are either producing or in the process of establishing a production base in China. Chinese markets are going to adopt the European regulations (Restrictions of Hazardous Substances, or RoHS) for chemicals such as FRs.

Israel

Of the approximately 548,000 t of global yearly bromine production in 2002, approximately 206,000 t (almost 38% of the total) are produced in Israel. A slightly larger quantity is produced in the United States. The overall estimated global growth of about 2% is also true for Israel. The sole Israeli producer of bromine is DSBG, which is part of the ICL Group. DSBG also produces bromine derivatives that have a wide range of applications. DSBG produces bromine from the Dead Sea, where its concentration ranges between 6.5 g/L in the southern basin and 12 g/L in the liquors remaining after potash production from the Dead Sea.

As previously stated, more than 90% of DSBG's sales are from exports. Therefore the current situation of lower prices for the main brominated products, along with regulatory pressures, threatens the main business of the company and its status as a major producer. DSBG is also a major manufacturer of the fumigant methyl bromide, which is being phased out. Therefore, DSBG, as well as other major producers, are seeking environmentally safe "green" products using bromine and bromine-containing chemicals.

Jordan

Because Jordan is situated on the eastern shores of the Dead Sea, it was only a matter of time before bromine production from Dead Sea brines began. A 25,000-tpy bromine plant was commissioned

in 2003. At full production capacity of 50,000 tpy, this plant would be able to replace the Albemarle production facilities in the United States. The production of brominated compounds (e.g., TBBA) will be able to commence very shortly after that time.

United States

It is difficult to find data on any definitive future demand estimates for bromine in the United States. Unofficial sources have predicted a modest yearly growth rate of about 1% to 2%. This prediction is based on the assumption that no new, major legislative restrictions will be placed on bromine chemical use in the foreseeable future. Bromine production from wells in Arkansas is diminishing at 2% to 3% per year, and higher production costs are anticipated. The major U.S. bromine chemical compounds companies (Albemarle and GLCC) are succeeding in finding alternative bromine sources. Albemarle finalized an agreement with a Jordanian partner to build the bromine plant previously described, with a maximum capacity of 50,000 tpy. GLCC completed an agreement with the Israeli company DSBG for the supply of bromine and brominated products. GLCC is developing alternative flame-retardant products based on tetrabromobenzoate esters as an alternative to the ecologically problematic penta-BDE FR used in the polyurethane sector. Albemarle is enlarging its TBBA (a leading BFR) production capacity. Both companies also have diversified their flame-retardant product lines by moving into nonhalogenated FRs through acquisitions.

OUTLOOK ACCORDING TO MAJOR USE

Flame Retardants

Over the last 10 years, the FR industry has been growing 3% to 5% annually (Chemical Products Synopses 2003). Unofficial figures from reliable sources indicate that the brominated section of the industry is growing at a similar pace. One of the reasons given for continued growth of the brominated segment is the increasingly stringent fire safety standards in place in Europe and the United States as a result of increasing fire-safety awareness. California, the most populous state in the United States, requires fire retardants in polyurethane foam mattresses, and proposed federal laws (e.g., American Home Fire Safety Act) would require similar actions.

Industry observers claim that there are about 50 different major BFRs. All major FRs (e.g., deca-PBDE, HBCD, TBBA, and penta-BDE) are currently undergoing risk assessments to see if they are in accord with the PBT (persistent, bioaccumulation, toxicity) criteria. Increasing efforts are being made to replace these with nonhalogenated FRs or with more environmentally friendly BFRs; that is, reactive ones that will not leach to the environment during use. Thus far, many of the introduced replacements have been different BFRs from the PBDEs that they were to replace. The strategy used by producers of brominated products is to shift from products under attack to products that are considered less environmentally problematic and are recyclable.

Drilling Fluids

The forecast for the clear brine fluids market depends on the general oil and gas drilling business climate, which itself is a highly fluctuating market. The mercurial behavior of this industry is illustrated by the steep decline in drilling activity between 1990 and 1993, followed by a significant increase in activity between 1994 and 2000. The market for calcium bromide in 2003 was approximately 90,000 t with a price of \$400 to 500/t; the market for zinc bromide brines was about 50,000 t. The market exhibits price erosion during periods of low demand, and competition from brine production from effluent hydrobromic acid.

The drilling fluids market is threatened by several factors:

- Consumption of brine fluids on a per-well basis will decline because of the expansion in reuse and recycling of brine fluids.
- Emerging ecological requirements are expected to have an accompanying new demand for “green” drilling fluids.

Biocides

The worldwide bromine-based biocide market is estimated to be about \$180 million with an annual growth rate of 4% to 5%. Approximately half of this is from industrial water treatment applications (cooling towers, paper mills, and so forth.) where the major products are bromine (hypobromous acid); bromochlorodimethylhydantoin (BCDMH); sodium bromide; ammonium bromide; 2,2-dibromo-3-nitropropionamide (DBNPA); 2-mercapto benzothiazole (MBT); and 1,4-bis(bromoacetoxy)-2-butene (BBAB). This market is divided as follows: North America and Canada, 50%; Europe, 25% to 35%; and the rest of the world, 15% to 25%. The other half goes mainly to the swimming pool and spa business as BCDMH and sodium bromide. In this case, the North American fraction is about 75% whereas the rest goes to southern Europe and Australia. The latter market fluctuates according to weather and the mood of the public.

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