

# Bromine, Inorganic Compounds

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## Abstract

This article contains a survey of the physical and chemical properties, methods of preparation or manufacture, and updated uses and applications for a number of classes of inorganic bromine compounds. The main classes included are (a) bromamines, (b) hydrogen bromide and hydrobromic acid, (c) metal bromides, (d) non-metal bromides, (e) bromine halides, (f) bromine oxides, (g) oxygen acids of bromine and their salts. This chapter also includes a brief discussion on applications of inorganic bromides in the area of drilling fluids, biocides, and concentrated aqueous solutions. Included are 122 references.

## 1. Introduction

The aim of this article is to provide a brief summary of physical and chemical properties of several classes of inorganic bromine compounds. The main classes of inorganic bromine compounds covered include (a) bromamines, (b) hydrogen bromide and hydrobromic acid, (c) metal bromides, (d) non-metal bromides, (e) bromine halides, (f) bromine oxides, (g) oxygen acids and their salts. Wherever possible, updated uses and applications have been cited for the specific compounds surveyed.

## 2. Bromamines

The bromamines are highly unstable compounds, having a tendency to explode at low temperatures, if they are isolated. Traces of these compounds can be formed when water containing small amounts of bromide and ammonia is chlorinated.

Monobromamine,  $\text{NH}_2\text{Br}$ , bromamide, [14519-10-9], was first prepared by reacting a dilute solution of bromine in anhydrous ether with a 50% excess of ammonia (in anhydrous ether) at  $-60^\circ\text{C}$  (1) according to the reaction



After the ammonium bromide and excess ammonia are removed, a pale straw-colored product solution remains. If the bromamine is isolated at low temperatures, it decomposes violently when its temperature is allowed to reach  $-70^\circ\text{C}$  (2). The bromamine reacts in ether with Grignard reagents to produce primary amines, ammonia, and nitrogen.

Dibromamine,  $\text{NHBBr}_2$  (bromimide) [14519-03-0], is prepared by adding an ether solution of ammonia to an excess of bromine (in ether) at a temperature of  $-50^\circ\text{C}$ , until the color of the bromine solution changes from red to yellow (1,3).



An ether solution of  $\text{NBr}_2$ , after the removal of ammonium bromide, is stable for several hours at  $-72^\circ\text{C}$ . When dibromamine reacts with Grignard reagents, primary and secondary amines are formed, together with ammonia and  $\text{N}_2$ . The disinfecting efficiency of dibromamine in water exceeds that of dichloramine (4).

At  $-78^\circ\text{C}$ ,  $\text{Br}_2$  and liquid ammonia form pale yellow-to-red solutions containing ammonium bromide and an equilibrium mixture of  $\text{NH}_2\text{Br}$  and violet  $\text{NBr}_3 \cdot 6\text{NH}_3$ .

Tribromamine,  $\text{NBr}_3$  (nitrogen tribromide) [15162-90-0], can be obtained as an ammoniate, ie,  $\text{NBr}_3 \cdot 6\text{NH}_3$ , by the reaction between bromine and ammonia below  $-70^\circ\text{C}$  (2). The tribromamine is predominant in water at  $\text{pH} < 8$  when 2–3 mol  $\text{Br}_2$  are added per mole ammonia (5); it may be extracted from water with chloroform.

### 3. Bromides

#### 3.1. Hydrogen Bromide

Hydrogen bromide,  $\text{HBr}$  (hydrobromic acid) [10035-10-6], is a colorless, corrosive gas that fumes strongly in moist air. It is extremely irritating to the eyes, nose, and throat. Some of the physical properties of anhydrous hydrogen bromide gas are summarized in Table 1.

**Table 1. Physical Characteristics of Hydrogen Bromide**

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mp $-86^\circ\text{C}$
bp $-67^\circ\text{C}$ (101.3 kPa)
liquid density 2.152 g/mL
heat of fusion at mp 29.8 kJ/kg (7.12 kcal/kg)
heat of vaporization at $-66.7^\circ\text{C}$ , 218 kJ/kg (52 kcal/kg)
heat capacity J/(kg · K) [cal/(kg · K)]
(i) solid at $-91^\circ\text{C}$ , 636 [152]
(ii) liquid 737 [176]
(iii) gas at $27^\circ\text{C}$ , 356 [85]
critical temperature $89.8^\circ\text{C}$
critical pressure 8510 kPa (84 atm)

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Hydrogen bromide gas is highly soluble in water, forming azeotropic mixtures whose compositions at various pressures have been determined (6). At normal atmospheric pressure, the boiling point of the azeotrope is 124.3°C and the HBr content is 47.63%. It freezes at about -11°C and has a density of 1.482 g/mL at 25°C. At very low temperatures, HBr forms hydrates with 1,2,3, and 4 molecules of water (7).

Methods for HBr gas preparation include

1. Reaction of a mixture of excess hydrogen with bromine vapor at a temperature of 500°C, or reaction of hydrogen and bromine at 375°C over platinized silica gel or platinized asbestos catalysts (8).
2. The reaction of bromine with sulfur or phosphorus and water. In the above-mentioned procedures, the HBr vapor that is formed is passed through hot, activated charcoal or iron to remove the free bromine (9), and is then either liquefied by cooling for shipment in cylinders or is absorbed into water.
3. Hydrogen bromide is obtained as a by-product during the bromination of aromatic compounds and separated by distillation. This hydrogen bromide is less pure and is usually used as a raw material for clear drilling fluids.

Laboratory methods for HBr preparation include

1. Distillation of HBr from potassium bromide and dilute sulfuric acid.
2. Reaction of bromine with sulfur dioxide and water followed by distillation.
3. For preparation of a dilute HBr solution, an alkali bromide solution can be passed through the hydrogen form of a cation-exchange resin that is suitable for dilute solutions.

Hydrobromic acid is one of the strongest mineral acids known. It is considered a more effective leaching agent than hydrochloric acid for some mineral ores because of its higher boiling point and stronger reducing action. Certain higher oxides such as ceric oxides are readily dissolved in HBr. The acid forms complexes with the bromides of several metals. Examples of such complexes are hydrogen tetrabromoferrate,  $\text{HFeBr}_4$ , amber [19567-68-1]; hydrogen tribromocuprate,  $\text{HCuBr}_3$ , violet [31415-59-5]. Bromine is highly soluble in concentrated aqueous hydrobromic acid.

***Safety and Environmental Considerations*** The liquids and vapors of HBr are highly corrosive to human tissue. The threshold limit value for hydrogen bromide gas in an 8-h day is 3 ppm time-weighted average. Inhalation of the vapor (when present at highly hazardous concentrations) is highly irritating to the nose and throat. Symptoms from HBr overexposure include coughing, choking, burning in the throat, wheezing, or asphyxiation. Ingestion of the HBr vapor causes severe burns of the mouth and stomach while skin contact can cause severe burns. In the case of liquid or vapor contact with the eyes, permanent damage may result. It is therefore imperative to employ the proper safety equipment when handling HBr including a safety shower and eye bath.

For 48% hydrobromic acid (which is corrosive to eyes, skin and mucous membranes) the following measures are suggested: (a) Eye contact: Hold eyelids apart, flush eyes promptly with large amounts of flowing water for at least 20 min. (b) Skin contact: Skin should be flooded with water. The skin should be washed thoroughly with mild soap and plenty of water for 15 min. (c) Inhalation: Remove person to fresh air. Keep person quiet and warm. Apply artificial respiration if needed. (d) Ingestion: If swallowed, wash mouth thoroughly with plenty of water and give water to drink. In all of the above cases, medical attention should be obtained immediately.

If a leak or spill occurs when working with HBr, the exposure to its vapors should be strictly avoided. If a high concentration of the hydrobromic acid is accidentally spilled, it should be diluted immediately with water to reduce its fuming before neutralization with soda ash or lime. Aqueous sodium hydroxide may also be used to neutralize the diluted acid. HBr also reacts with metals to produce highly explosive hydrogen gas.

Most metals, concrete, and other construction materials are corroded by HBr. Suitable materials of construction include some fiber glass-reinforced plastics, some chemically resistant rubbers, polyvinyl chloride (PVC), Teflon, polypropylene and ceramic-, rubber-, and glass-lined steel. Metals that are used include Hastelloy B, Hastelloy C, and titanium. The Hastelloys are only suitable at ambient temperatures. Hydrogen bromide under pressure in glass at or above room temperature can attack the glass, resulting in unexpected shattering.

Technical 48 and 62% acids range from colorless-to-light yellow liquids, which are available in drums or tank trailers and tank car quantities. They are classified under DOT regulations as corrosive materials. Anhydrous HBr is available in cylinders under its vapor pressure ( $\sim 2.4$  MPa or 350 psi) at 25°C. It is classified as a nonflammable gas.

### *Uses and Applications*

1. Hydrogen bromide is used in the manufacture of inorganic bromides. Metal hydroxides or carbonates are used for the neutralization.
2. Hydrogen bromide is also a raw material in the synthesis of alkyl bromides from alcohols.
3. Hydrobromination of olefins. The addition can take place by an ionic mechanism, usually in a polar solvent according to Markovnikob's rule to yield a secondary alkyl bromide. By using a free-radical catalyst in aprotic, nonpolar solvents, dry HBr reacts with an olefin to produce a primary alkyl bromide as the predominant product. Primary alkyl bromides are used in synthesizing other compounds and are 40–60 times as reactive as the corresponding chlorides (10).
4. Hydrogen bromide adds to acetylene to form vinyl bromide or ethylidene bromide, depending on the stoichiometry.
5. Hydrogen bromide cleaves acyclic and cyclic ethers.
6. Hydrogen bromide adds to the cyclopropane group by ring opening.

7. Addition of hydrogen bromide to quinones produces bromohydroquinones.
8. Hydrogen bromide and aldehydes can be used to introduce bromoalkyl groups into various molecules, eg, bromoethylation of aromatic nuclei (10).
9. In the petroleum industry, HBr serves as an alkylation catalyst.
10. Hydrogen bromide is claimed as a catalyst in the controlled oxidation of aliphatic and alicyclic hydrocarbons to ketones, acids, and peroxides (11,12).
11. Applications of HBr with NH<sub>4</sub>Br (13) or with H<sub>2</sub>S and HCl (14) as promoters for the dehydrogenation of butene to butadiene.
12. Hydrogen bromide is used in the replacement of aliphatic chlorine by bromine - in the presence of an aluminum catalyst.
13. Hydrogen bromide also finds use in the electronics industry.
14. Hydrogen bromide is used to make a catalyst for PTA production or is used as the catalyst itself.

### 3.2. Metal and Non-Metal Bromides

**Properties** Physical characteristics of common metal bromides are summarized in Table 2 (15). Table 3 presents data for the solubilities in water for selected metal bromides as a function of temperature.

**Table 2. Physical Properties and Characteristics of Selected Metal Bromides**

Compound	mp, °C	bp, °C	d <sub>4</sub> <sup>25</sup>	Other characteristics
sodium bromide	747	1390	3.26	bitter, salty hygroscopic white solid
potassium bromide	730	1435	2.75	bitter, salty hygroscopic white solid
calcium bromide	730 <sup>a</sup>	810	3.35	white, hygroscopic, salty crystal
lithium bromide	550	1265	3.46	eye and skin exposure can irritate
ammonium bromide	452 (subl.)		2.43	white, yellow hygroscopic solid
zinc bromide	394	650	4.20	metallic taste, hygroscopic solid
aluminum bromide	97.5	263 <sup>b</sup>	3.0	white, yellow hygroscopic solid

cadmium  
bromide                    568                    1136

<sup>a</sup> Some decomposition occurs.

<sup>b</sup> At a pressure of 99.6 kPa. To convert kPa to mmHg multiply by 7.5.

**Table 3. Solubilities of Various Inorganic Bromides in Water as Function of Temperature<sup>a</sup>**

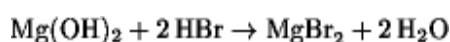
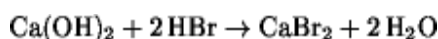
t, °C	0	20	40	60	80
	58.8	62.7	67.5	69.1	71.0
	44.2	47.5	51.4	54.1	54.1
	35.1	39.6	43.2	46.2	48.8
	37.3	42.6	47.3	51.2	53.9
	55.5	58.8	68.1	73.5	74.7
	79.6	81.6	85.5	86.1	86.6
	49.5	50.3	51.6	52.8	—
	46.0	50.6	55.2	60.0	64.5
	48.5	50.3	52.4	54.3	56.5
	53.0	56.7	59.1	60.4	60.6

<sup>a</sup> Solubilities in % by weight

Other physical properties have been redetermined in recent years for some of the above metal bromide solutions. Some examples include

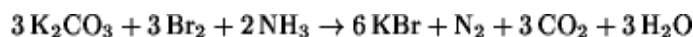
1. Densities and sound velocities were measured (16) for aqueous solutions of zinc bromide, calcium bromide, and sodium bromide in the ionic strength range of 0–0.8 at 25°C.
2. Viscosities and densities of aqueous solutions of LiBr and ZnBr<sub>2</sub> were also measured for both single salt (17) and two-salt solutions (18). For the single-salt solutions, the densities were presented in tabular form and as 10-parameter correlations.
3. Densities of 0.1, 0.5 and 1.0 mol·kg<sup>-1</sup> solutions of sodium and potassium bromide were determined at 1°K temperature intervals from a temperature of 277.15°K to a temperature of 343.15°K (19).

**Manufacture** The metal bromides are generally prepared by the reaction of hydrogen bromide with the metals, hydroxides, carbonates, or oxides of the metals. For the specific cases of alkali and alkaline earth bromides, the procedure involves the neutralization of the corresponding hydroxide or carbonate with hydrobromic acid, evaporation of excess water, and crystallization. For example,

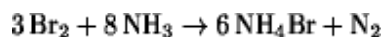


Both CaBr<sub>2</sub> and MgBr<sub>2</sub> may be extracted from concentrated brines, using a suitable solvent. Both solvent extraction processes were developed by IMI (TAMI). MgBr<sub>2</sub> is extracted using higher alcohols (20) while CaBr<sub>2</sub> is extracted with a composite solvent. The calcium bromide process was tested on a semicommercial scale by DSBG (21) with positive results.

An alternative preparation used is the van der Meulen process where bromine and a reducing agent such as ammonia, formic acid, or carbon is used in place of the hydrobromic acid (22). The reaction using ammonia is given below



Ammonium bromide [12124-9-9] is prepared on a commercial scale by the reaction of bromine with aqueous ammonia according to the following equation

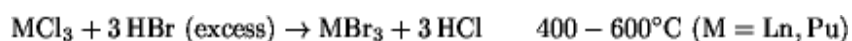


Some other routes (23) to metal bromides that have been considered include

1. High temperature bromination of metal oxides, sometimes in the presence of CBr<sub>4</sub> or carbon, to assist in the removal of oxygen. For example, Nb<sub>2</sub>O<sub>5</sub> can be

converted to NbBr<sub>5</sub> using CBr<sub>4</sub> as the brominating agent at a temperature of 370°C. Similarly, Ta<sub>2</sub>O<sub>5</sub> can form TaBr<sub>5</sub> in the presence of carbon and Br<sub>2</sub> above 460°C.

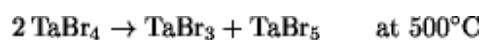
2. A closely related route is a halogen exchange, usually in the presence of an excess of the halogenation agent



3. Reductive halogenation of the higher bromide with the parent metal, another metal or hydrogen



4. Thermal decomposition or disproportionation to yield the lower bromide



Metal bromide solutions can be prepared on a laboratory scale using the reaction of the appropriate carbonate or sulfate with barium bromide.

A more recent process suggested (24) for the preparation of inorganic bromide salts is the reaction of the respective chloride salt with 1,2-dibromoethane (DBE). The reaction is reportedly carried out under convenient phase-transfer catalytic conditions. The process used to produce calcium bromide is based on mixing aqueous calcium chloride with DBE at 90°C in the presence of the phase-transfer catalyst didecyldimethylammonium bromide (2%).

Other procedures that have appeared more recently in the chemical literature are described here briefly:

1. A recent patent (25) claimed an inexpensive process for the production of lithium bromide having a desired purity level, where LiCl or LiSO<sub>4</sub> are used as raw materials. Either of the above-mentioned lithium salts is reacted with NaBr or KBr in an aqueous, semiaqueous or organic medium. The precipitated salts are removed so that a LiBr solution of the desired purity can be achieved. The process claims the avoidance of the use of highly acidic materials, thus reducing the cost of the raw materials and the need for specialized equipment.
2. Another method (26) offered for the production of an ammonium bromide, and optionally, a calcium bromide brine, uses sodium bromide brine as the raw material. The process consists of introducing ammonia and carbon dioxide into a sodium bromide brine to form a product solution of ammonium bromide.



ammonium bicarbonate, and a sodium bicarbonate precipitate. Following removal of the sodium bicarbonate solids from the product solution, two options are available: (a) Ammonium bromide can be recovered from the solution by evaporative crystallization. (b) Calcium bromide can be produced by the addition of calcium hydroxide or calcium oxide to the product solution, following removal of the  $\text{NaHCO}_3$  solids.

3. Zinc by-products (containing low grade zinc oxide from industrial products) are used (27) for the manufacture of clear brine fluids by mixing the zinc feedstock (containing metal impurities) with  $\text{HBr}$  at pH 3.5–4.5 to produce an impure zinc bromide solution. Metal impurities are removed by precipitation and filtration of the manganese and iron impurities at pH 3–5, and then the zinc bromide solution is concentrated. The solution is then contacted with elemental zinc (zinc shot) at 40–80°C to cement out nickel, lead, cadmium, copper, mercury, and cobalt under an alkalinity of <1.0% zinc oxide. It is preferable to contact the zinc bromide solution with the zinc metal in multiple passes through packed column systems.
4. Two additional recent Chinese processes deal with the production of ammonium bromide (28) and potassium bromide (29). The process for ammonium bromide is initiated by the preparation of a solution of stoichiometric amounts of sodium bicarbonate and urea. A stoichiometric amount of bromine is added slowly to the solution, with continuous stirring. After the removal of Fe, filtering, and evaporation, reagent grade ammonium bromide is crystallized. The process for potassium bromide is similar: The reaction of bromine with potassium carbonate and urea is the basis of the process. The first step of the process involves the addition of  $\text{K}_2\text{SO}_4$  to the potassium carbonate solution, followed by heating to 80°C. After the lead-containing precipitate is removed by filtration, the bromine and urea are added, and the temperature and pH are adjusted to 30°C and 6.0–6.5, respectively. Potassium bromide is recovered by recrystallization after reduction of volume of the reacting solution by evaporation. The sulfate can be removed from the solution by addition of  $\text{BaBr}_2$ .

The production of the nonmetal bromides is accomplished through the reaction of the nonmetal with hydrogen bromide or bromine at an elevated temperature. Uses and physical properties of selected inorganic nonmetal bromides are listed below.

Boron tribromide,  $\text{BBr}_3$  [10294-33-4]

Physical characteristics: specific gravity 2.64, mp  $-46^\circ\text{C}$ , bp  $91.3^\circ\text{C}$ . Volatile liquid.

Uses: (1) In diborane and ultrahigh purity boron manufacture. (2) Arylacetone boron tribromide aldol condensation cyclization (30).

Phosphorus pentabromide,  $\text{PBr}_5$  [7789-69-7]

Physical characteristics: mp  $83.8^\circ\text{C}$ , bp  $> 106^\circ\text{C}$ . Red-yellow solid.

Uses: (1) Brominating agent: Converts organic acids to acyl bromide. (2) Converts phenols and sec-alcohols to bromides (31,32).

Phosphorus tribromide,  $\text{PBr}_3$  [7789-60-8]

Produced by the reaction between bromine and yellow phosphorus in  $\text{PBr}_3$  at  $130^\circ\text{C}$ .

Physical characteristics: Specific gravity 2.85, mp  $-40^\circ\text{C}$ , bp  $173^\circ\text{C}$ . Colorless liquid.

Uses: (1) Converts alcohols to alkyl bromides (33). (2) Catalyst in specific organic reactions.

Selenium tetrabromide,  $\text{SeBr}_4$  [7789-65-3]

Physical characteristics: Decomposes at  $75^\circ\text{C}$ . Red-brown crystals.

Uses: (1) Dopant for a photoreceptor for electrophotography (34). (2) Additive for a rapid bright silver electroplating bath (35).

Silicon tetrabromide,  $\text{SiBr}_4$  [7789-66-4]

Produced from reaction of silicon and  $\text{Br}_2$  vapor  $> 600^\circ\text{C}$ .

Physical characteristics: mp  $5^\circ\text{C}$ , bp  $153^\circ\text{C}$ . Colorless liquid.

Use: Production of high purity silicon (36).

Tellurium tetrabromide,  $\text{TeBr}_4$  [10031-27-3]

Physical characteristics: Specific gravity 4.31, mp  $380 \pm 6^\circ\text{C}$ , bp  $421^\circ\text{C}$  (decomposes).

Orange crystals.

Use: Catalyst for synthesis of acids (37,38).

Thionyl bromide,  $\text{SOBr}_2$  [507-16-4]

Produced by passing  $\text{HBr}$  into thionyl chloride with cooling, without the introduction of moisture. Physical characteristics: Specific gravity 2.69, mp  $-52^\circ\text{C}$ , bp  $39^\circ\text{C}$  (2 kPa). Orange-yellow liquid.

Use: Brominating agent in organic chemistry, eg, converts alcohols to alkyl bromides (39).

Tribromosilane,  $\text{SiHBr}_3$  [7789-57-3]

Produced by reaction of metallurgical grade silicon with  $\text{SiBr}_4$  (tetrabromosilane) at  $600\text{--}800^\circ\text{C}$  in hydrogen atmosphere. Physical characteristics: mp  $-73.5^\circ\text{C}$ , bp  $112^\circ\text{C}$ .

Colorless liquid.

Use: Production of high purity silicon (36).

**Applications** The main applications of inorganic bromides are in drilling fluids, biocides, photography, pharmaceuticals, catalysts, and brominating agents.

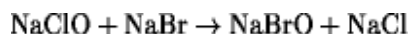
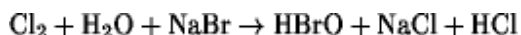
**Drilling Fluids** (*see also Drilling Fluids*) The calcium, zinc, and sodium bromides find extensive applications in the oil and gas drilling industry for high density, clear drilling completion, packer, and workover fluids. They find extensive use in deep, high pressure oil and gas wells. These fluids are advantageous in that they do not plug the formation in workover and completion operations, as conventional drilling muds can. Higher production rates and longer lifetimes are the result. In the United States, calcium bromide

is the highest volume bromide salt used for this application, followed closely by zinc bromide and sodium bromide. Sodium bromide finds specialized use where calcium/zinc bromides can cause minimal swelling or in strata containing carbon dioxide. Bromine-based completion fluids are used for offshore and onshore drilling.

Calcium bromide is available for oil fields as a 95% minimum purity solid or as a 52–54% aqueous solution (specific gravity 1.70–1.71 at 15.5°C). Zinc bromide is available as a 75% aqueous brine having a specific gravity of 2.4. Also marketed is a zinc bromide/calcium bromide brine for use when prevailing pressures require densities up to 2.3 g/mL (19.2 lb/US gal). Assay for this mixture is 18–21% CaBr<sub>2</sub>, 53–58% ZnBr<sub>2</sub>, and its maximum crystallization point is –7°C.

**Biocides** Ammonium bromide and sodium bromide are used to control microbial, fungal, and algal growth in industrial water systems such as cooling towers, pulp, and paper mills, once through cooling water and in wastewater disinfection. Sodium bromide, as a biocide (40% solution), is typically applied in conjunction with chlorine gas (Cl<sub>2</sub>), 12.5% sodium hypochlorite (NaClO), sodium dichloro-*s*-triazinetrione, or sodium trichloro-*s*-triazinetrione to form the active biocidal species hypobromous acid (HBrO), or a predefined mixture of hypochlorous/hypobromous acid (40).

For example,



At the elevated pH levels commonly found in use in today's cooling water programs, hypobromous acid exhibits much greater biocidal efficacy when compared to chlorine. Hypobromous acid is effective in the presence of ammonia and can help to minimize TRO (total residual oxidant) levels in order to enable the end user to meet stricter environmental discharge regulations. Sodium bromide activated by an oxidizer is used also for pools and spas sanitation.

**Concentrated Aqueous Solutions** A number of nondrilling fluid applications have been suggested in recent years for concentrated zinc bromide brines and related bromide solutions. Some of these are referred to briefly.

1. Filaments of polyketones can be formed into various fibers using concentrated aqueous zinc bromide or lithium bromide solutions as solvents for dissolving the polyketones (41).
2. A process (42) was described for the electrophilic substitution of an aromatic compound, where an aromatic compound, a precursor of the desired substituent and an aqueous reagent containing a high concentration of zinc bromide are the

constituents of the reacting mixture. In certain instances, a water soluble compound, lithium bromide, is added in order to enhance the effectiveness of the catalysis and to increase the reaction yield.

3. Use of concentrated zinc bromide in water and aqueous polar organic solvents for the separation of alcohols from hydrocarbons and alkyl halides (43).
4. Separation of a nonanediol and nonol mixture in methylene chloride by extraction of a zinc bromide-containing water-methanol system (44).
5. Zinc bromide solutions have been suggested (45) as a component of a multiphase mixture in hydraulic systems.

Information on uses of wide range of metal bromides is summarized below.

**Aluminum bromide**,  $\text{AlBr}_3$  [7727-15-3]

Uses: Anhydrous compound used as acid catalyst in Friedel–Crafts reactions, olefin polymerizations, hydrocarbon isomerization, and olefin alkylation of aromatics.

**Ammonium bromide**,  $\text{NH}_4\text{Br}$  [12124-97-9]

Uses: (1) A biocide to control microbial, fungal, and algal growth in industrial water systems. (2) For light-sensitive photographic emulsions and developing solutions. (3) Process engraving and lithography. (4) Wood fireproofing. (5) Corrosion inhibitor. (6) Flame retardant for chipboard. (7) Sedative. (8) Textile finishing.

**Barium bromide**,  $\text{BaBr}_2$ [10553-31-8]

Uses: (1) Reactant for bromide manufacture. (2) X-ray storage phosphor (46).

**Beryllium bromide**,  $\text{BeBr}_2$  [7787-46-4]

Use: Adhesive for polyvinyl alcohol (47).

**Bismuth bromide**,  $\text{BiBr}_3$  [7787-58-8]

Uses: (1) Claimed: catalyst for dehydrating cyclohexanol to cyclohexene (48). (2) Claimed: Part of solid electrolyte in primary lithium batteries (49). (3) Polymerization of methyl methacrylate monomer to yield transparent resins (50). (4) Catalyst for benzylation of aliphatic alcohols. (51).

**Calcium bromide**,  $\text{CaBr}_2$  [7789-41-5]

Uses: (1) Applications in oil and gas well completion, workover, and packer brines (52–54% calcium bromide, specific gravity >1.7). (2) Water treatment. (3) Photography. (4) Gravity separation fluid. (5) Electrical conductivity fluid

**Cerous bromide**,  $\text{CeBr}_3$  [14457-87-5]

Use: In molten salt bath for reduction of uranium oxide by magnesium (52).

**Cesium bromide**,  $\text{CsBr}$  [7787-69-1]

Uses: (1) X-ray fluorescent screens. (2) Spectrometer prisms. (3) Adsorption cell windows. (4) Claimed: Optical fibers.

**Chromous bromide**,  $\text{CrBr}_2$  [10049-25-9]

Use: Chromizing.

**Chromic bromide**,  $\text{CrBr}_2$ , [10031-25-1]

Use: Catalyst for polymerizing olefins (53).

**Cobaltous Bromide**,  $\text{CoBr}_2$  [7789-43-7]

Use: (1) In hydrometers. (2)  $\text{CoMnBr}_n$  catalyst for organic reactions (54,55).

**Cupric bromide**,  $\text{CuBr}_2$ [7789-45-9]

Uses: (1) Intensifier in photographic chemicals. (2) Brominating agent in organic syntheses (56,57). (3) Catalyst in production of acrylic acid, olefins, and vinyl chloride. (4) Humidity indicator. (5) Wood preservative. (6) Solid electrolyte batteries.(7) Stabilizer for acetylated polyformaldehyde.

**Cuprous bromide**,  $\text{CuBr}$  [7787-70-4]

Uses: (1) Catalyst for organic reactions (58,59). (2) Water-activated  $\text{CuBr}$  battery (60).

**Ferric bromide**,  $\text{FeBr}_3$  [10031-26-2]

Uses: (1) Catalyst for  $\text{C}_{60}$  bromination (61). (2) Catalyst for organic reactions, particularly in brominations of aromatics.

**Ferrous bromide**,  $\text{FeBr}_2$  [7789-46-0]

Use: Component of metamagnets (62).

**Gold tribromide**,  $\text{AuBr}_3$  [10294-28-7]

Use: Claimed: Sensor component for halogenated gases (63).

**Lithium bromide**,  $\text{LiBr}$  [7750-35-8]

Uses: (1) Absorption-type chillers (55% solution) (64). (2) Heat pump (65). (3) Dehumidifier. (4) Lithium - bromine battery. (5) Sedative.

**Magnesium bromide**,  $\text{MgBr}_2$  [7789-48-2]

Uses: (1) Used in organic syntheses (66,67). (2) Sedative, anticonvulsant.

**Manganese bromide**,  $\text{MnBr}_2$  [13446-03-2]

Uses: (1) Catalyst: In formation of aromatic aldehydes from alkylbenzenes (68) and phthalic acids from xylenes (69). (2) Claimed: Catalyst in ammoxidation conversion of (*o*)-xylene to phthalimide (70). (3) Preparation of substituted haloalkylopyrazoles (71).

**Mercurous bromide**,  $\text{Hg}_2\text{Br}_2$  [10031-18-2]

Use: Reacts with  $\text{HBr}$  to form hydrogen quantitatively (72).

**Nickel bromide**,  $\text{NiBr}_2$  [13462-88-9]

Uses: (1) Catalyst: Dimerization of butadiene (73). (2) Catalyst: Condensing butadiene onto ring systems and benzyl ketones (74,75). (3) Catalyst: oxidation of sec-alcohols to ketones (76). (4) Preparation of biaryls from aryl halides (77).

**Palladium bromide**,  $\text{PdBr}_2$ , [13444-94-5]

Use: Catalyst for various carbonylation reactions (78,79).

**Platinum bromide**, PtBr<sub>2</sub> [13455-12-4]

Use: Dehydrodimerization catalyst for boron hydrides and carboranes (80,81).

**Potassium bromide**, KBr [7758-02-3]

Uses: (1) For light-sensitive photographic emulsions and developing solutions. (2) Used in process engraving and lithography. (3) Pharmaceutical preparations. (4) Heat stabilizer for nylon. (5) Controls epileptic seizures in dogs.

**Praseodymium bromide**, PrBr<sub>3</sub> [13536-53-3]

Uses: (1) In molten salt bath for reduction of uranium oxide by magnesium (52). (2) Light filter for cathode ray tube (82).

**Rhodium bromide**, RhBr<sub>3</sub> [15608-29-4]

Use: Catalyst: Carbonylating methanol to acetic acid (83).

**Rubidium bromide**, RbBr [7789-39-1]

Uses: (1) Component of X-ray intensifier screens (84). (2) Antiferromagnets (85).

**Silver bromide**, AgBr [7785-23-1]

Uses: (1) Photography. (2) Topical antiinfective. (3) Astringent.

**Sodium bromide**, NaBr [7647-15-6]

Uses: (1) Oxidizing biocide used to control microbial, fungal, and algal growth in industrial water systems. (2) Oil well completion fluid. (3) Bleaching agent (used with oxidizer). (4) For light-sensitive photographic emulsions and developing solutions. (5) Leaching agent, in combination with Br<sub>2</sub>, for gold/silver ores (86). (6) Pharmaceutical preparations.

**Stannic bromide**, SnBr<sub>4</sub> [7789-67-5]

Use: In metallurgical separation of minerals (87).

**Stannous bromide**, SnBr<sub>2</sub> [10031-24-0]

Use: Claimed: Catalyst for preparation of lubricant antioxidant (88).

**Strontium bromide**, SrBr<sub>2</sub> [10476-81-0]

Uses: (1) Anticonvulsant. (2) Chemical heat pump (89).

**Thallium bromide**, TlBr [7789-40-4]

Use: Claimed: Component in radiographic image conversion panels (90).

**Titanium bromide**, TiBr<sub>4</sub> [7789-68-6]

Use: Catalyst for olefin polymerizations (91).

**Tungsten bromide**, WBr<sub>6</sub> [13701-86-5]

Use: Catalysts for polymerizing olefins (53).

**Zinc bromide**, ZnBr<sub>2</sub> [7699-45-8]

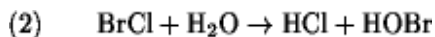
Uses: (1) Used to make silver bromide collodion emulsions (photography). (2) Radiation shielding. (3) Gravity separation. (4) Electrical conductivity fluid. (5) Storage battery electrolyte for electric vehicles and load leveling applications (92).

(6) Used in completion, workover, and packer brines in oil well drilling and maintenance.

#### 4. Bromine Halides

Bromine is capable of forming a number of bromine halide compounds under varying process conditions. In general, these compounds have properties intermediate between those of the parent halogens. The most important of these are described below.

**Bromine chloride**, BrCl [13863-41-7]: This compound is formed when bromine and chlorine react reversibly in the liquid and vapor phases at room temperature. Where an equimolar mixture of these halogens is reacted, ~60% of the mixed halogens are present as BrCl (93). The bromine chloride is a dark red, fuming, irritating liquid having an mp  $-66^{\circ}\text{C}$  and bp  $5^{\circ}\text{C}$ . BrCl has uses in organic synthesis involving the addition across olefinic double bonds to produce bromochloro compounds, and for aromatic brominations, where an aromatic bromide and HCl are produced. Some other characteristic reactions for BrCl are

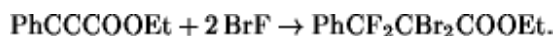


BrCl also finds use as a disinfectant in wastewater treatment (94) where it enjoys the following advantages over chlorine: activity maintained over a wider pH range, more rapid disinfection, effective at lower residual concentrations, and lower aquatic toxicity (95). Specific uses in water treatment: Effluent streams from sewage plants and cooling water towers. In addition, bromine chloride has applications as a brominating agent in the preparation of fire-retardant chemicals, pharmaceuticals, high density brominated liquids, agricultural chemicals, dyes, and bleaching agents.

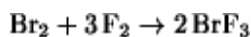
The time-weighted average concentration of bromine chloride should not exceed 0.1 ppm for an 8-h day. Suitable materials of construction for shipping and storing BrCl are low carbon steel or nickel, or its alloys, such as Monel (95).

**Bromine monofluoride**, BrF [13863-59-7]: The monofluoride may be prepared by direct reaction between bromine and fluorine. Because of its high tendency to

disproportionate, it has never been prepared in its pure form (96). However, the BrF can be prepared in situ by the reaction of bromine with silver fluoride in benzene (97) or by the reaction of *N*-bromoacetamide and hydrofluoric acid in ether (98). BrF adds to simple alkenes at room temperature to give trans-addition products. BrF also adds to various alkynes to give the family of compounds containing CF<sub>2</sub>CB<sub>r</sub>2

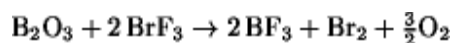


**Bromine trifluoride**, BrF<sub>3</sub> [7787-71-5]: The trifluoride can be formed by the reaction between gaseous fluorine and liquid bromine at a temperature of 200°C (99):

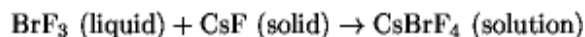


The BrF<sub>3</sub> can be purified by distillation to give a pale straw-colored liquid.

Bromine trifluoride undergoes vigorous reaction with water, organic compounds, and metals. (It is somewhat less vigorous a fluorinating agent than the corresponding trifluoride of chlorine.) Reaction of BrF<sub>3</sub> with oxides often evolves oxygen quantitatively



The high specific conductivity of the BrF<sub>3</sub>, ie,  $> 8 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$ , is due to its autoionization in the liquid state to the BrF<sub>2</sub><sup>+</sup>BrF<sub>4</sub><sup>-</sup> species. This Lewis acid–base character is thus demonstrated by the ability of BrF<sub>3</sub> to dissolve in a number of halide salts, eg, CsF according to the reaction



Bromine trifluoride is a useful solvent for those ionic reactions that need to be carried out under highly oxidizing conditions. As a strong fluorinating agent, it finds use in organic syntheses and in the formation of inorganic fluorides. Bromine trifluoride is highly toxic and corrosive to all tissues. Rail shipments of bromine trifluoride require “Oxidizer” and “Poison” labeling.

**Bromine Pentafluoride**, BrF<sub>5</sub> [13863-59-7]: Bromine pentafluoride can be formed



either by (1) the reaction of bromine with excess fluorine above 150°C or by (2) the reaction of BrF<sub>3</sub> vapor and gaseous fluorine at 200°C (99). Small-scale preparation of BrF<sub>5</sub> can be achieved by the fluorination of KBr at a temperature of 25°C. Analogous to the trifluoride, the pentafluoride reacts with alkali fluorides, eg, MF to form MBrF<sub>6</sub> salts. BrF<sub>5</sub> is also used as a fluorinating agent in organic syntheses (100–102) and as the oxidizer component of some rocket propellants. It can fluorinate silicates at 450°C as follows



BrF<sub>5</sub> is highly toxic and corrosive to the skin. It requires the “Oxidizer” label for rail shipments and the “Corrosive” label for air shipments.

The two bromine fluorides—the trifluoride and pentafluoride—are available commercially.

A summary of the physical properties of the Br—F compounds is given in Table 4 below (103).

**Table 4. Properties of Bromine–Fluorine Binary Compounds**

	mp (°C)	bp (°C)	Specific conductivity at 25°C ( $\Omega^{-1} \text{cm}^{-1}$ )	Structure
BrF	–33	20	—	—
BrF <sub>3</sub>	9	126	$>8.0 \times 10^{-3}$	planar; distorted T
BrF <sub>5</sub>	–60	41	$9.1 \times 10^{-8}$	square pyramidal

Materials of construction for the bromine fluorides include nickel, Monel metal, or teflon.

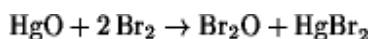
**Iodine bromide**, IBr [7789-33-5], is a black solid (mp 41°C, subl 50°C) that is more stable than bromine monochloride. It is formed by the reaction between bromine and iodine. There is also evidence for the existence of a tribromo species, iodine tribromide IBr<sub>3</sub> [7789-58-4]. These iodine–bromine compounds are soluble in

carbon tetrachloride and acetic acid and are used as halogenating agents (104,105).

## 5. Bromine Oxides

None of the bromine oxides are stable at ordinary temperatures and none are considered to be of any practical importance.

**Dibromine oxide**, bromine monoxide, Br<sub>2</sub>O [21308-80-5]. This compound is a dark-brown solid that is moderately stable at -60°C (mp -17.5°C with decomposition). Br<sub>2</sub>O is a bent symmetrical molecule like Cl<sub>2</sub>O, with a C<sub>2v</sub> symmetry. It is formed by (1) the low temperature decomposition of BrO<sub>2</sub> in vacuum or by (2) the reaction of Br<sub>2</sub> vapor with HgO. The latter reaction is carried out in a carbon tetrachloride or fluorotrichloromethane solvent



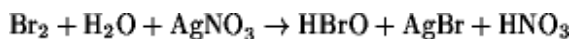
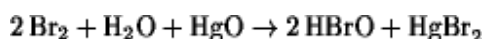
Excess mercuric oxide and mercuric bromide are then removed by filtration. The solution obtained can be used in brominations. Br<sub>2</sub>O oxidizes iodine to I<sub>2</sub>O<sub>5</sub>, benzene to 1,4-quinone and yields OBr<sup>-</sup> in alkaline solutions.

**Bromine dioxide**: This compound is a yellow solid formed by the oxidation of Br<sub>2</sub> in CF<sub>3</sub>Cl at -78°C with ozone. BrO<sub>2</sub> is thermally unstable above -40°C, and decomposes violently at ~0°C. Slower warming of BrO<sub>2</sub>, as mentioned above, yields Br<sub>2</sub>O. Alkaline hydrolysis of BrO<sub>2</sub> leads to disproportionation to bromate and bromide. A recent study (106) claims that BrO<sub>2</sub> is a largely or totally a mixture of Br<sub>2</sub>O<sub>3</sub> and Br<sub>2</sub>O<sub>5</sub>.

## 6. Oxygen Acids and Salts

The oxygen acids of bromine are unstable strong oxidizing agents, which exist only at ambient temperatures in solution.

**Hypobromous acid**, HBrO [7486-26-2]. This compound can be prepared by reacting either mercuric oxide or silver nitrate with bromine water according to the following reactions (107):



To obtain more concentrated solutions from the products of the above reactions, the weak HBrO solution is distilled under vacuum following removal of AgBr or HgBr<sub>2</sub> by filtration. An alternative method proposed for obtaining concentrated solutions was to carry out the mercuric oxide reaction in Freon 11, without using water, to yield a solution of bromine monoxide, which was then filtered and hydrolyzed. HBrO is a weak acid that is only slightly ionized. Its dissociation constant is  $1.6 \times 10^{-9}$  at 25°C. Hypobromous acid is used as a strong bactericide and as a water disinfectant.

The salts of hypobromous acid, referred to as hypobromites, undergo slow disproportionation to bromate and bromide



Cobalt, nickel, and copper catalyze the disproportionation reaction (108), so that these impurities should be avoided.

Alkali metal hypobromites are generally prepared by reacting bromine with an alkali hydroxide (eg, sodium hydroxide) in aqueous solution at a temperature < 0°C



At temperatures of 50–80°C, quantitative yields of BrO<sub>3</sub><sup>-</sup> are obtained according to the reaction

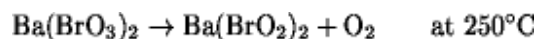
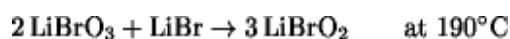


Pure crystalline hydrates such as NaOBr · 5H<sub>2</sub>O [13824-96-9] and KOBr · 3H<sub>2</sub>O [13824-97-0] were not described until the work of Scholder and Kraus (109). Solid alkaline earth hypobromites such as CaBr(OBr) [67530-61-4] have been known since the early twentieth century. The hypobromites find use as bleaching and desizing agents in the textile industry.

**Bromous acid**, HOBrO [7486-26-2]: In general, halite ions and halous acids do not arise during the hydrolysis of halogens. Thus, the existence of bromous acid is therefore considered to be in doubt (96).

**Sodium bromite**, NaBrO<sub>2</sub> [7486-26-2]: This compound is available in the United States at a solution concentration of ~10%, and is used as a desizing agent in the textile industry. Sodium bromite has been synthesized as 99.6% pure NaBrO<sub>2</sub>·3H<sub>2</sub>O, and is available commercially in Europe. This compound is made from a concentrated hypobromite solution at pH 11–12, at a temperature <0°C. After ammonia has been added to the solution to decompose any hypobromite that remains after reaction, a yellow sodium bromite trihydrate is isolated through concentration and filtration. The sodium salt is stable and can be stored for long periods of time.

**Barium bromite**, Ba(BrO<sub>2</sub>)<sub>2</sub> [14899-01-5]; **potassium bromite**, KBrO<sub>2</sub> [76908-17-3]; and **lithium bromite** LiBrO<sub>2</sub> [14518-92-4]: These compounds can be prepared in a similar way to that described for the sodium salt under vacuum at 0°C (110). Anhydrous lithium and barium bromite have been prepared by heating bromate salts (111)



Such compounds are stable for at least 3 months. The bromites find industrial application as desizing agents for textiles and in water treatment.

**Bromic acid**, (HBrO<sub>3</sub> [7789-31-3]: This compounds can be prepared by (1) the reaction of alkali bromates with dilute sulfuric acid, or (2) by the electrolysis of bromine in bromic acid solution with platinum or lead dioxide anodes (112). Another preparation method is by the passage of an alkali bromate solution (~0.5 M) through a cation exchanger in the H<sup>+</sup> -form (113,114). The acid coming from ion exchange can be concentrated (in vacuum) to ~50%. The 50% solution begins to decompose at around 40°C while more concentrated solutions are not stable. HBrO<sub>3</sub> is a strong acid (pK < 0). It is also a strong oxidant, with a standard potential of 1.47 V for the reaction HBrO<sub>3</sub> → 0.5 Br<sub>2</sub> (in acid medium).

The industrially important bromates—sodium and potassium bromate—are commonly produced by the electrolytic oxidation of the corresponding aqueous bromide solution in the presence dichromate at a temperature of 65–70°C (115). Cathodes may be made of stainless steel or copper while the anode is usually lead dioxide or iron. The bromate formed is then crystallized by cooling the hot solution, after removing it from the cell. The mother liquor is treated with more bromide and recycled.

Another method for producing bromate salts is the reaction of alkali hydroxide or carbonates with bromine at elevated temperatures, as cited previously. In this case, sodium bromide is also produced along with the bromate. The relatively high sodium bromide solubility permits the bromates to be recovered by cooling and filtration. The commercial sodium bromate product is available at a 99.5% minimum assay. An Israeli patent (116) describes the manufacture of bromate–bromide mixtures.

A recent patent for sodium bromate production (117) is comprised of dissolving sodium carbonate in water, passing bromine and chlorine gases into the solution, filtering the hot solution to remove sodium chloride, and cooling the filtrate to 5–10°C to obtain a crude sodium bromate. The crude product is then redissolved in hot water and recrystallized in the temperature range of 5–10°C.

**Sodium bromate**, NaBrO<sub>3</sub> [7789-38-0]: This compound is a strong oxidizing agent, which can cause fires upon contact with organic materials. As the bromates are a source of active oxygen, when either heated, subjected to shock or acidified, they represent potential fire and explosion hazards. The bromates are usually packed in polyethylene-lined filter drums. Metal drums have also been used for packaging. The bromates are considered quite stable in storage.

Some physical characteristics and uses are listed for selected bromates:

1. **Sodium bromate**: Colorless crystal or powder. specific gravity 3.34, mp 381°C (decomposes with oxygen evolution). Water solubility at 25°C is 28.39 g/100 g solution while at 80°C, the solubility is 43.1 g/100 g solution. Uses: (a) Neutralizer–oxidizer in hair wave preparations. (b) Used in mixtures with sodium bromide in gold mining applications. (c) Used in applications in textile bleaching.
2. **Potassium bromate**, KBrO<sub>3</sub> [7758-01-2]: White crystals or powder, specific gravity 3.27, decomposes at ~327°C. Water solubility at 25°C is 7.53 g/100-g solution while at 80°C, the solubility is 25.4 g/100-g solution. This bromate is a powerful oxidizing agent, either in the pure state or when blended with magnesium carbonate. Uses: (a) Flour treatment to improve baking characteristics. (b) Hair wave solutions. (c) Malting of beer. (d) Cheese manufacture. (e) Used as an analytic standard.
3. **Barium bromate**, Ba(BrO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O [10326-26-8]: Exists as white crystals. Specific gravity 4.0. Loses water of crystallization at 180–200°C and decomposes at ~270°C. Produced by reaction between bromine and barium hydroxide. This bromate is used as a corrosion inhibitor.

Some of the characteristic reactions of aqueous bromates include

1. Reaction with hydrogen peroxide to yield O<sub>2</sub>.
2. Reaction with PH<sub>3</sub> to yield phosphoric acid.

3. Reaction with HBr to yield Br<sub>2</sub>.
4. Reaction with XeF<sub>2</sub>, F<sub>2</sub> (alkali) to yield BrO<sub>4</sub><sup>-</sup>.
5. Reaction with OCl<sup>-</sup> (slow) to yield ClO<sub>4</sub><sup>-</sup>.
6. Reaction with nitrous acid to yield nitric acid.

**Perbromic acid** HBrO<sub>4</sub> [19445-25-1]: This compound is a strong acid, which is completely dissociated in aqueous solutions. This acid is generally prepared by passing sodium perbromate solution through a cation-exchange resin, which is in the hydrogen form. Perbromic acid solutions, at concentrations above 6 M (55%), are air unstable. They are believed to undergo an autocatalytic decomposition that is catalyzed by some metal ions, eg, Ag<sup>+</sup> and Ce<sup>4+</sup>. Perbromic acid is very similar to perchloric acid, having little oxidizing activity in dilute solution but being quite capable of reacting violent when concentrated. A 3 M perbromic acid solution attacks stainless steel, a 6 M solution at 100°C rapidly oxidizes Mn<sup>2+</sup> to MnO<sub>4</sub><sup>-</sup> and a 12 M solution explodes on contact with cellulose.

The perbromates were first prepared by E. Appelman at the Argonne National Laboratory in 1968 by oxidizing a bromate either electrolytically or with xenon difluoride (118). A fluorination procedure was reported a year later by Appelman (119) to produce larger quantities of the perbromates. The newer method consisted of introducing fluorine into strongly basic solutions of bromates. The normal oxidation potential of the BrO<sub>4</sub><sup>-</sup> / BrO<sub>3</sub><sup>-</sup> couple in acid solution is 1.74 V. Appelman and co-workers(120) reported the thermodynamic properties of perbromate and bromate ions, as well as the effects of photolysis and pulse-radiolysis on perbromate in aqueous solutions (121,122). Perbromic acid can also be used to prepare perbromate salts.

**Sodium perbromate**, NaBrO<sub>4</sub> [33497-30-2]: This compound is highly soluble in water while **potassium perbromate**, KBrO<sub>4</sub> [22207-96-1], is soluble only to the extent of ~0.2 M at room temperature.

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