SODIUM HALIDES

1. Sodium Bromide

Sodium bromide [7647-15-6], NaBr, the most common and available alkali bromide, is a salt of hydrobromic acid (see Bromine compounds). Sodium bromide crystallizes from aqueous solution as a dihydrate[13466-08-5], $NaBr{\cdot}2H_2O$, below 51°C. Above 51°C, it crystallizes as the anhydrous compound. Crystals of the dihydrate belong to the monoclinic system and have lattice parameters $a = 659$ pm, $b = 1020$ pm, and $c = 651$ pm. The anhydrous crystal belongs to the cubic system, $a = 596$ pm.

1.1. Properties.

Other physical properties of the anhydrous salt are listed in Table 1. The anhydrous salt is hygroscopic but not deliquescent.

Sodium bromide has a very high water solubility. At 25°C a saturated solution contains 48.6% sodium bromide by weight. Values for the solubility at several temperatures are known (1). Three parameter equations for calculating the solubility in terms of mole fraction of both the anhydrous and dihydrate salts are available (2). Convenient for calculating the solubility in weight percent of sodium bromide in water at various temperatures, t in °C, are as follows:

$$0\,^{\circ}\mathrm{C} \le t < 51^{\circ}\mathrm{C}$$

$$\mathrm{soly}_{\mathrm{NaBr}} = 44.335 + 0.1536t + 6.752 \times 10^{-4}t^2$$

$$51^{\circ}\mathrm{C} \le t \le 100^{\circ}\mathrm{C}$$

$$\mathrm{soly}_{\mathrm{NaBr}} = 52.207 + 3.945 \times 10^{-2}\,t - 1.307 \times 10^{-4}t^2$$

Both equations give the weight percent of sodium bromide in an aqueous saturated solution to within ±0.02 percentage units. One gram of sodium bromide dissolves in about 16 mL of ethanol and 6 mL of methanol (3).

1.2. Manufacture.

Small quantities of pure sodium bromide can be prepared by neutralizing solutions of either sodium hydroxide [1310-73-2] or sodium carbonate [497-19-8] using hydrobromic acid [10035-10-6] which is free of bromine, followed by evaporation and crystallization.

Commercial quantities of sodium bromide are usually prepared by adding excess bromine [7726-95-6] to a solution of sodium hydroxide, evaporating to dryness, and treating with a reducing agent such as formic acid [64-18-6] or activated carbon [7440-44-0] to reduce sodium bromate [7789-38-0] to sodium bromide. Some sodium bromide is recovered as a by-product of the bromination of organic materials. Grades of sodium bromide available are chemically pure (CP), crystal, powdered, commercial, pure, highest purity, and National Formulary (NF). Sodium bromide is available in crystalline or powdered forms and in solution (4).

1.3. Health and Safety Factors.

Sodium bromide is moderately toxic by ingestion and can affect the gastrointestinal and central nervous systems and the skin (6). Ingestion of large amounts in a single dose causes immediate abdominal pain. Gastrointestinal effects include nausea and vomiting, foul breath, anorexia, weight loss, dehydration, and constipation. Neurological effects include headache, apathy, slurred speech, impaired memory and intellectual capacity, and drowsiness. Skin effects include acneiform, rash, pustules, and ulcers (7). Inhalation of sodium bromide dusts may cause mucous membrane and bronchial irritation.

The LD_{50} for sodium bromide taken orally by rats is 3.5 g/kg body weight, and the TD_{LO} orally in rats is 720 mg/kg. RTECS lists data on reproductive effects in male and female rats. Sodium bromide is listed in the TSCA Inventory, the Canadian Domestic Substances list (DSL), the European Inventory of Existing Commercial Chemical Substances (EINECS), the Japanese Existing and New Chemical Substances (ENCS), and the Korean Existing Chemicals list (ECL). It is not regulated by the U.S. Department of Transportation.

1.4. Uses. The oil and gas drilling industry is a principal consumer of sodium bromide. Because of its high solubility in water, clear brine fluids of densities up to 1.547 g/cm^3 (12.9 lb/gal) at 25°C can be obtained. These are used directly or in blends with other clear brine fluids for well completions or workovers. Densities of sodium bromide brines containing up to 50 wt% sodium bromide and at temperatures to 100°C have been tabulated (8). The density in g/cm^3 of sodium bromide brines at temperatures in °C can be calculated from the following equation when $0°\mathrm{C} \leq t \leq 100°\mathrm{C}$.

$$\text{density} = (0.991 - 7.30 \times 10^{-3} \times \ \text{wt\%}\,\text{NaBr} + 4.08 \times 10^{-4}\,t)^{-1}$$

An increasingly important use of sodium bromide is as a biocide, particularly in industrial cooling water towers and in swimming pool water treatment, replacing the more hazardous chlorine [7782-50-5] (see Water, treatment of swimming pools, spas, and hot tubs). Sodium bromide is usually converted to elemental bromine, bromine chloride [13863-41-7], or hypobromite through the use of activators such as hypochlorites and chlorinated isocyanurates. Some studies have suggested that bromine is three times more effective than chlorine in controlling algae in cooling towers (9). Also, the trend in cooling water treatment to operate at higher pH to minimize corrosion, leads to larger amounts of algae. Bromine is more effective under these higher pH conditions (10).

Other applications of sodium bromide include use in the photographic industry both to make light-sensitive silver bromide [7785-23-1] emulsions and to lower the solubility of silver bromides during the developing process; use as a wood (qv) preservative in conjunction with hydrogen peroxide (11); as a cocatalyst along with cobalt acetate [917-69-1] for the partial oxidation of alkyl side chains on polystyrene polymers (12); and as a sedative, hypnotic, and anticonvulsant. The FDA has, however, indicated that sodium bromide is ineffective as an over-the-counter sleeping aid for which it has been utilized (13). An easy process for the manufacture of hydrobromic acid and sodium bisulfate from sodium bromide has been reported (14).

2. Sodium Fluoride

2.1. Properties. Sodium fluoride [7722-88-5], NaF, is a white, free-flowing crystalline powder, mp 992°C, bp 1704°C, with a solubility of 4.2 g/100 g water at 10°C, and 4.95 g/100 g water at 93.3°C. The purity of the commercial material is about 98%.

2.2. Manufacture. Sodium fluoride is normally manufactured by the reaction of hydrofluoric acid and soda ash (sodium carbonate), or caustic soda (sodium hydroxide). Control of pH is essential and proper agitation necessary to obtain the desired crystal size. The crystals are centrifuged, dried, sized, and packaged. Reactors are usually constructed of carbon brick and lead-lined steel, with process lines of stainless, plastic or plastic-lined steel; diaphragm, plug cock, or butterfly valves are preferred.

The salt is packaged in 45-kg multiwall bags or fiber drums of 45, 170, or 181 kg. It is available in both powdered and granular forms with densities of 1.04 and 1.44 g/cm^3 (65 and 90 lb/ft^3), respectively. Only the powdered grade is authorized by and registered with the EPA for use in pesticide formulations, with the further proviso that it must be tinted blue or green, or otherwise discolored. The word poison appears on all labels together with first-aid information. This product should be stored in a cool, dry environment (15).

2.3. Health and Safety Factors. Both sodium fluoride and sodium bifluoride are poisonous if taken internally. Dust inhalation and skin or eye contact may cause irritation of the skin, eyes, or respiratory tract, and should be avoided by the use of proper protective equipment (6). Primary route for occupational exposure is by inhalation.

ACGIH TLV TWA and OSHA PEL TWA for sodium fluoride is 2.5 mg $(F)/m^3$ (6).

2.4. Uses. Fluoridation of potable water supplies for the prevention of dental caries is one of the principal uses for sodium fluoride (see Water, municipal water treatment). Use rate for this application is on the order of 0.7 to 1.0 mg/L of water as fluoride or 1.5 to 2.2 mg/L as NaF (16). NaF is also applied topically to teeth as a 2% solution (see Dentifrices). Other uses are as a flux for deoxidizing (degassing) rimmed steel (qv), and in the resmelting of aluminum. NaF is also used in the manufacture of vitreous enamels, in pickling stainless steel, in wood preservation compounds, casein glues, in the manufacture of coated papers, in heat-treating salts, and as a component of laundry sours.

3. Sodium Bifluoride

3.1. Properties. Sodium bifluoride (sodium acid fluoride, sodium hydrogen fluoride) [1333-83-1], $NaHF_2$ or $NaF{\cdot}HF$, is a white, free-flowing fine granular material. Its solubility in water is 3.7 g/100 g solution at 20°C, and 16.4 g/100 g at 80°C. It decomposes at temperatures above 160°C to give sodium fluoride and hydrogen fluoride. Commercial material is ca 99% pure. To prevent the formation of irritating dust, wetted products, containing 85–90% $NaHF_2$ and 10–15% water, are also in use.

3.2. Manufacture. The same reactants are used for manufacture as for sodium fluoride. An excess of acid is required to crystallize the bifluoride. The crystals are dewatered, dried, sized, and packaged. Cooling of the reaction is necessary to avoid over-heating and decomposition. Reactors and auxiliary equipment are the same as for sodium fluoride.

The dried salt is shipped in 45-kg multiwall bags and in 57-, 170-, and 180-kg fiber drums. Densities range from ca 0.70 g/cm^3 (44 lb/ft^3) to 1.2 g/cm^3 (75 lb/ft^3) for crystalline material.

3.3. Uses. Sodium bifluoride, by itself or in conjunction with other materials, is a good laundry sour because, in the concentrations used, it does not create a pH below 4.0 and thus causes no damage to textile fibers, although it removes iron stains. Leather (qv) bleaching and cleaning of stone and brick building faces are other uses for this material (17).

4. Sodium Iodide

Sodium iodide [7681-82-5], NaI, occurs as colorless crystals or as a white crystalline solid. It has a salty and slightly bitter taste. In moist air, it gradually absorbs as much as 5% water, which causes caking or even liquefaction (deliquescence). The solid slowly becomes brown when exposed to air because some iodide is oxidized to iodine. Water solutions are neutral or slightly alkaline and gradually become brown for the same reason. Aqueous solutions are stabilized with respect to oxidation by raising the pH to 8–9.5 (see IODINE AND IODINE COMPOUNDS).

4.1. Properties. Sodium iodide crystallizes in the cubic system. Physical properties are given in Table 2 (18). Sodium iodide is soluble in methanol, ethanol, acetone, glycerol, and several other organic solvents. Solubility in water is given in Table 3.

Below 65°C, sodium iodide is present in aqueous solutions as hydrates containing varying amounts of water. When anhydrous sodium iodide is dissolved in water, heat is liberated because of hydrate formation, eg, $\Delta H = -174.4$ kJ/mol (-41.7 kcal/mol), when the dihydrate is formed. At room temperature, sodium iodide crystallizes from water as the dihydrate [13517-06-1], $NaI \cdot H_2O2H_2O$, in the form of colorless prismatic crystals.

4.2. Manufacture. Bulk production of *United States Pharmacopeia* (USP) and reagent grades is based on the reaction of sodium carbonate or hydroxide with an acidic iodide solution, typically hydriodic acid or a metal iodide. After removal of chemical impurities, the solution is filtered and concentrated. Evaporation gives the anhydrous NaI. Controlled cool-down produces either the dihydrate or the pentahydrate [81626-33-7].

Essentially no waste products are formed in the USP process if hydriodic acid and either sodium hydroxide or sodium carbonate are used as reactants. Water results from use of the former; a mole equivalent quantity of carbon dioxide is produced from the latter reagents. Higher quality grades may require some purification steps which may result in wastes from the treatment. Disposal of these impurities must then be carried out.

4.3. Health and Safety Factors. Sodium iodide is moderately toxic by ingestion, intravenous, and intraperitoneal routes. When heated to decomposition, it emits toxic fumes of I^- and Na_2O (6).

4.4. Uses. The principal use of sodium iodide is in scintillation crystals, which are used for gamma-ray counters (19), and in medicine as the detectors in computer-assisted tomography (CAT) scan and positron emission tomography (PET) equipment (20). A small amount is used in the wet extraction of silver, in iodized salt (see FOOD ADDITIVES), animal feeds to prevent hoofrot (see FEEDS AND FEED ADDITIVES), photographic chemicals, as an antiinfectant for body drapes in medicine, and in the manufacture of organic chemicals. It has also been used in cloud seeding and in halogen discharge lamps.

USP XXII specifies that sodium iodide contains 99–101.5% NaI, calculated on an anhydrous basis (21). It is used interchangeably with potassium iodide as a therapeutic agent, except where sodium ion is contraindicated (see POTASSIUM COMPOUNDS). Intravenous sodium iodide formulations have been used for a variety of diseases, from thyroid deficiency to neuralgia (see THYROID AND ANTITHYROID PREPARATIONS). However, these solutions are no longer listed in the *NF XVII* (21), indicating that their therapeutic value has not been satisfactorily demonstrated.

Veterinary uses of sodium iodide include the treatment of horses, cattle, sheep, swine, and dogs for various afflictions (see VETERINARY DRUGS).

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Table 1. **Properties of Sodium Bromide**

Property	Value
molecular weight	102.89
melting point, °C	755
boiling point, °C	1390
density, g/cm^3	3.203
refractive index, $n^{25}{}_D$	1.6412
heat of fusion, J/g[a]	254.9
ΔH_f, kJ/mol[a]	−361.414
S, J/(mol·K)[a]	86.82
heat capacity, (J/mol·K)[a,b]	$47.92 + 1.331 \times 10^{-3}$ T

[a] To convert J to cal, divide by 4.184.

[b] Temperature, *T*, is in Kelvin.

Table 2. **Physical Properties of Sodium Iodide**[a]

Property	Value
mol wt	149.895
mp, °C	651
bp, °C	1304
d_4^{25}, g/cm^3	3.667
specific heat, J/(kg·K)[b]	
at 0°C	350
50°C	360

[a] Ref. 18.

[b] To convert J to cal, divide by 4.184.

Table 3. **Aqueous Solubility of Sodium Iodide**

Temperature, °C	NaI g/100 g H_2O
0	158.7
20	178.7
40	205.0
60	256.8
70	294
80	296
100	302
140	321