Kirk-Othmer Encyclopedia of Chemical Technology.

SODIUM SULFIDES

The sodium sulfides have many diverse uses and are expected to experience modest demand growth into the twenty-first century. Sodium sulfide [1313-82-2], Na_2S, mol wt 78.05; sodium hydrosulfide [16721-80-5] (sodium sulfhydrate, sodium bisulfide, sodium hydrogen sulfide), NaHS, mol wt 56.06; and sodium tetrasulfide [12034-39-8], Na_2S_4, mol wt 174.24, are somewhat interchangeable in many applications. These compounds are used in the pulp (qv) and paper (qv) industries, in mining and leather (qv) tanning applications, as chemical intermediates, and in dye production (see Dyes and dye intermediates; Minerals recovery and processing). Environmental applications of these sulfides, including heavy metal precipitation from wastewater and the removal of nitrogen oxides from emissions, are of particular interest to many industrial chemical consumers.

1. Sodium Hydrosulfide

1.1. Properties

Pure sodium hydrosulfide is a white, crystalline solid, mp 350°C, sp gr 1.79. The commercial product, available in flake form at approximately 73% strength, is yellow in color and highly deliquescent. The color of the commercial product varies under the influence of minor changes in manufacturing and is not an indicator of purity beyond the range of a few parts per million. The melting point of the commercially available flake is approximately 52°C; the bulk density is approximately 0.64 g/cm^3. The average water of hydration may be expressed as $NaHS\cdot 0.81H_2O$. The flake is highly soluble in water, alcohol, or ether (1).

The heat of formation of NaHS is -237.6 kJ/mol (-56.79 kcal/mol); the heat of solution is 15.9 kJ/mol (10.7 kcal/mol) (2). In aqueous solution NaHS has an alkaline pH. Boiling points, densities, and freezing points for solutions of varying strengths are shown in Figure 1 (1). When exposed to air, sodium hydrosulfide undergoes autoxidation and gradually forms polysulfur, thiosulfate, and sulfate. It also absorbs carbon dioxide, forming sodium carbonate.

1.2. Manufacture

Sodium hydrosulfide was first produced in Germany and then in the United States in 1938. Production is closely related to the supply of hydrogen sulfide, which reacts with sodium hydroxide to form NaHS. Hydrogen sulfide can also be obtained by the reaction of hydrogen and sulfur, as a by-product of the carbon disulfide process, barium and strontium chemical manufacturing, or from desulfurizing petroleum fractions (see Sulfur removal and recovery). High purity NaHS production is very dependent on a supply of high purity H_2S and NaOH. The reaction produces high yields based on both reactants.

$$H_2S + NaOH \longrightarrow NaHS + H_2O$$

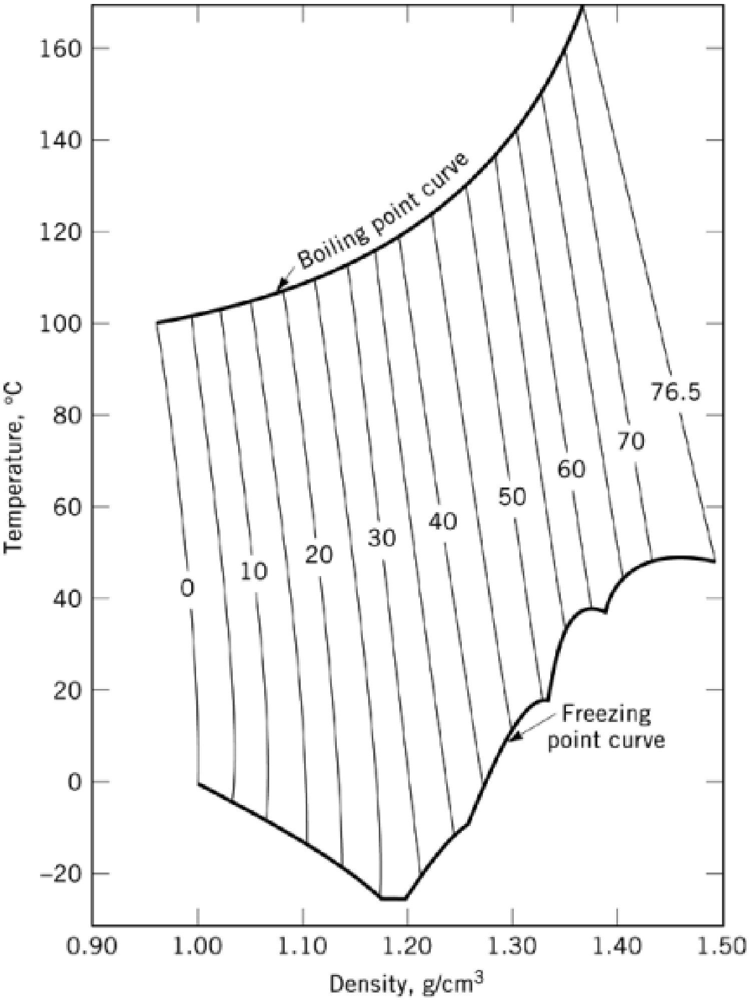

Fig. 1. Density of sodium hydrosulfide solutions in water, where the numbers on the vertical lines represent concentrations of NaSH in wt % (1).

NaHS, marketed as 71.5–74.5 wt % flakes and 43–60 wt % liquor in the high purity grades, is also available as 10–40 wt % liquor from the oil refining desulfurization process. NaHS is sold commercially in 22.7-kg bags, 181.4-kg drums, in tank trucks, and in rail cars.

1.3. Economic Aspects and Uses

Production and sales values for high purity sodium hydrosulfide are listed in Table 1. These figures exclude the low purity material produced by oil refiners, believed to be sold primarily to pulp mills. Estimates of uses of NaHS in the United States for 1994 are as shown (3, 4):

Use	Percentage
pulp processing (kraft)	40
ore flotation	28
chemicals and dyes	15
leather processing	12
miscellaneous, includes rayon and cellophane desulfurization	5

Use of NaHS in ore flotation (qv) has decreased over the years owing to the substitution of more environmentally sound methods, but this usage may fluctuate along with copper (qv) production. Use in dye production has remained constant, whereas the use of NaHS in pulp processing is increasing as the demand for paper products increases. Modest growth in the leather (qv) tanning sector has resulted from strengthening of demand in the automotive industry and increases in leather exports (3). The engineering plastic poly(phenylene sulfide) uses NaHS as a raw material and has the potential of becoming a significant growth area in this market (5) (see Engineering plastics; Polymers containing sulfur).

Table 1. U.S. Production and Prices of Sodium Hydrosulfide

Year	Production, $t \times 10^3$	Price, \$/t
1965	39.9	118
1970	26.3	133
1975	21.8	236
1980	41.7	277
1985	56.2	454
1991	45.4	530

In many applications sodium hydrosulfide and sodium sulfide are interchangeable. Where either chemical may be used, 28% less sodium hydrosulfide is required by weight to achieve a given level of sulfidity and is therefore the more economical choice. If desired, the sodium hydrosulfide can be converted to sodium sulfide by the addition of sodium hydroxide:

$$\mathrm{NaHS + NaOH \longrightarrow Na_2S + H_2O}$$

Sodium sulfides are very effective as heavy metal precipitants owing to the extremely low solubilities exhibited by metal sulfides. Sulfides, effective for precipitating most of the priority pollutant metals, which include Ag, As, Be, Cd, Cu, Cr, Hg, Ni, Pb, Se, Tl, and Zn, have been adopted by the EPA as a best available technology (BAT) application (6). Sulfide application offers several advantages over the conventional hydroxide processes. The lower solubility of sulfide metals provides improved metal removal efficiency (Fig. 2). Sulfide precipitation of metals remains effective over a wide pH range without sacrifice to minimum solubilities. It is effective in treating complexed metals, and the final disposal of the precipitated metal sulfides is easier and safer than the hydroxide process owing to lower acid (pH 5) leaching characteristics (9).

2. Sodium Sulfide

2.1. Properties

Pure sodium sulfide is a white, crystalline solid, mp 1180°C, sp gr 1.856. The commercial product is available in flake form at approximately 60% strength, is a light tan-to-yellow color, and is deliquescent. Figure 3 shows

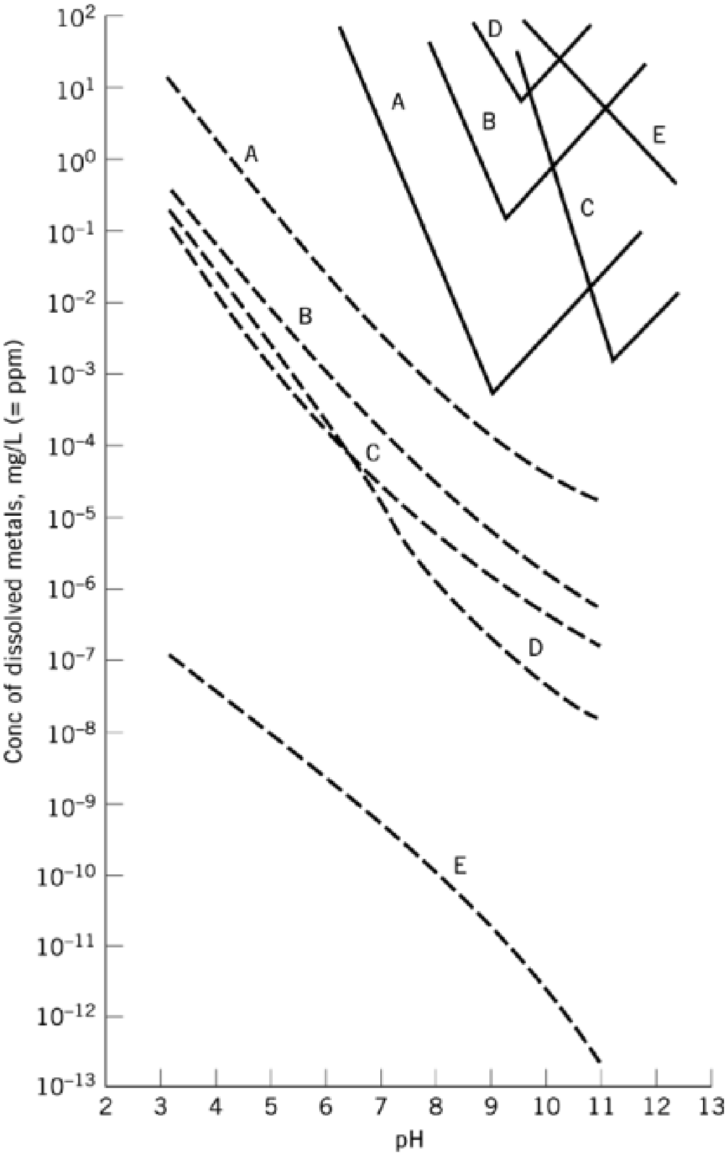

Fig. 2. Solubilities of (—) metal hydroxides, $M(OH)_2$, and (— — —) metal sulfides, MS, as a function of pH, where A–D correspond to M = Cu, Zn, Cd, and Pb, respectively (7). For E, the formulas are (—) AgOH and (— — —) Ag_2S. Curves for metal sulfides are based on experimental data listed in Reference 8.

the boiling points, densities, and freezing points for various solution strengths (1). The heat of formation for the crystalline state is -373 kJ/mol (−89.1 kcal/mol), and the heat of solution is -63.5 kJ/mol (-15.2 kcal/mol) (10). In solution, Na_2S is strongly alkaline. The bulk density of the commercially available flake is approximately 0.64 g/cm^3. The flake exists as a concentrated mixture of several hydrated forms and contains 59–62 wt % sodium sulfide. The average water of hydration may be expressed as $Na_2S{\cdot}2.71H_2O$. Sodium sulfide crystallizes from aqueous solutions as the nonahydrate [1313-84-4], $Na_2S{\cdot}9H_2O$. The flake is readily soluble in water, slightly

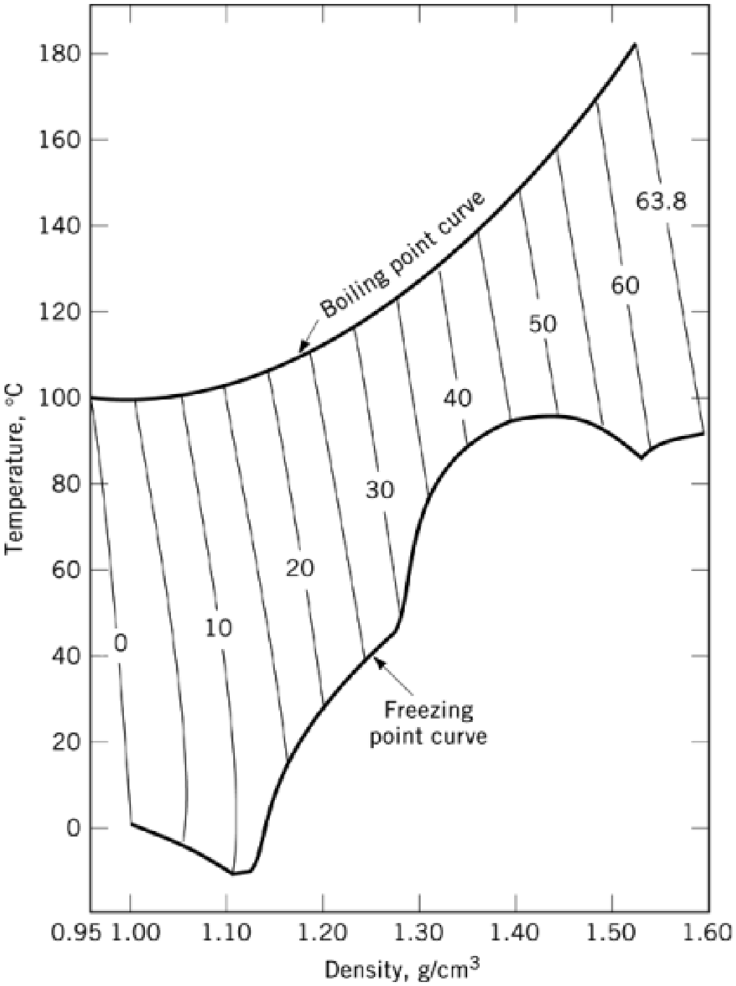

Fig. 3. Density of sodium sulfide solutions in water, where the numbers on the vertical lines represent concentrations of Na_2S in wt % (1).

soluble in alcohol, and insoluble in ether. When exposed to air, sodium sulfide undergoes autoxidation to form polysulfur, thiosulfate, and sulfate. It also absorbs carbon dioxide to form sodium carbonate. Reactions with strong oxidizing agents form elemental sulfur.

2.2. Manufacture

The oldest method for producing Na_2S is by the reduction of sodium sulfate with carbon in a refractory oven at 900–1000°C. Whereas this method is no longer used commercially in the United States, a variation is used to produce sodium sulfide captively during kraft pulp processing to replace lost sodium and sulfur values that were initiated into the system by merchant-supplied sodium sulfide. In this method, sodium sulfate is added to the system in the recovery furnace, where it is reduced by carbon from the wood pulp to produce sodium sulfide.

$$Na_2SO_4 + 4\ C \longrightarrow Na_2S + 4\ CO \qquad (3)$$

$$Na_2SO_4 + 4\ CO \longrightarrow Na_2S + 4\ CO_2 \qquad (4)$$

One commercial process for producing sodium sulfide is as a by-product of barium carbonate production (see Barium compounds). Barite ore, $BaSO_4$, is reduced with carbon at 800°C to produce crude barium sulfide (black ash), which is then leached to dissolve the barium sulfide in solution. The solution is then reduced using sodium carbonate to produce barium carbonate, leaving a weak sodium sulfide solution as the by-product. The sodium sulfide solution may then be concentrated and flaked or crystallized.

$$BaS + Na_2CO_3 \longrightarrow BaCO_3 + Na_2S$$

Another process involves two steps. Sodium hydrosulfide from equation 1 reacts with sodium hydroxide to yield sodium sulfide (eq. 2). Concentration by evaporation to 60 wt % is practiced unless concentrated sodium hydroxide is used.

2.3. Economic Aspects and Uses

Production and pricing information for Na_2S through 1991 are listed in Table 2. U.S. production of sodium sulfide increased rapidly from 1965 through 1972 and then began to decrease. The last year that the U.S. Bureau of the Census released official production figures was in 1974 because at that time there were only three producers of sodium sulfide. Estimates indicate that 1991 production fell to the levels of the late 1950s. List prices have increased since 1974 as sulfur and sodium hydroxide prices have increased.

Table 2. U.S. Production and Prices of Sodium Sulfide

Year	Production, $t \times 10^3$	Flake price, $/t
1965	39	113
1970	68	124
1972	80	127
1974	64	132
1991	25	476[a]

[a] Ref. 11.

About 65% of 1990 U.S. sodium sulfide usage was in the leather industry for dehairing hides before tanning. This application is similar to that of sodium hydrosulfide. The production of miscellaneous chemicals, which took up to 25% in 1990, included the production of polysulfide elastomers and plastics as well as a variety of organic chemicals. In the dye industry, Na_2S is used as a solvent for water-soluble dyes and as a reducing agent. In ore flotation, the mining industry uses Na_2S to form insoluble metal sulfides of copper, lead, molybdenum, nickel, and cobalt. Other uses of Na_2S include wood (qv) digestion, the preparation of lubrication oils, and in the preparation of rayon and cellophane by removing sulfur.

Technology has been developed for the absorption of nitrogen oxides from gas streams via sodium sulfide scrubber systems. The nitrogen oxide streams from various processes can be converted to elemental nitrogen, whereas the sulfide is oxidized to the sulfate ion (12).

2.4. Sodium Tetrasulfide

Sodium tetrasulfide is prepared by the reaction of sodium sulfide with sulfur. The 34 wt % solution is normally dark red, solidifies at -15 to -9°C, boils at 113°C, and has a specific gravity at 15.5°C of 1.268. The chemical formula is written Na_2S_4, but the product is better regarded not as a compound but as a mixture of sodium sulfide with free, elemental sulfur, ie, $Na_2S{\cdot}S_3$. Sodium tetrasulfide is available in 249.5-kg drums of 34 wt % solution. It is used in leather processing, dye manufacturing, wastewater treatment, in metals finishing, ore manufacturing, and in lubricant manufacturing. No commercial polysulfide of significance is produced other than the tetrasulfide.

3. Analysis

A double end point, acid–base titration can be used to determine both sodium hydrosulfide and sodium sulfide content. Standardized hydrochloric acid is the titrant; thymolphthalein and bromophenol blue are the indicators. Other bases having ionization constants in the ranges of the indicators used interfere with the analysis. Sodium thiosulfate and sodium thiocarbonate interfere quantitatively with the accuracy of the results. Detailed procedures to analyze sodium sulfide, sodium hydrosulfide, and sodium tetrasulfide are available (1).

4. Health and Safety

The combination of organic matter and the sodium sulfides can cause combustion to occur. Zinc, aluminum, and copper should not be used where these can come into direct contact with any of the sodium sulfides. Personnel handling sodium sulfides must be equipped with goggles, a full face shield, and rubber or plastic protective clothing. Chemical cartridge escape respirators should be available at all storage and use locations, owing to the potential for hydrogen sulfide formation. The sodium sulfides are similar to sodium hydroxide and other alkalies as corrosive substances on animal tissues. Contact with skin can be very irritating and is especially harmful to soft tissues.

Inhalation of sodium hydrosulfide mist causes irritation of the respiratory tract and possible systemic poisoning. Hydrogen sulfide gas, which may be given off when acid is present, causes headache, dizziness, nausea, and vomiting. Continued exposure can lead to loss of consciousness, respiratory failure, and death. Extreme care should be taken to avoid mixing any of the sodium sulfides and acids. Storage areas and sewers should be segregated so as to avoid any possibility of these chemicals being mixed. It is recommended that a continuous-monitoring hydrogen sulfide gas detection and alarm system be installed in any area where hazardous levels of hydrogen sulfide gas may occur. Concentrations of 4.3 to 46% hydrogen sulfide by volume in air are explosive and self-ignite above 260°C. Burning hydrogen sulfide gas produces toxic sulfur dioxide. Firefighters must wear self-contained breathing apparatus to prevent breathing sulfur dioxide gas (13).

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Related Articles

Mineral recovery and processing; Sulfur compounds