# SODIUM SULFATES AND SULFIDES

## 1. Sodium Sulfates

**1.1. Introduction.** Sodium sulfates are industrially important commonly sold in three forms (Table 1). In the period 1970 to 1981, one million metric tons were consumed annually in the United States. Since then, demand has declined. In 2003, consumption dropped to 363,000 t and the estimate for 2004 is 330,000 t. In the United States, sodium sulfate is used principally (46%) in the soap and detergent industries, pulp and paper uses account for 13%, textiles, 12%, glass, 11% carpet fresheners,7%, and miscellaneous uses, 11%.

About half of all sodium sulfate produced is by a synthetic by-product of rayon, dichromate, phenol, or potash (see Potassium compounds). Sodium sulfate made as a by-product is referred to as synthetic. Sodium sulfate made from mirabilite, thenardite, or naturally occurring brine is called natural sodium sulfate.

In 2004, United States sodium sulfate production was split 50:50 from natural deposits and recovered by-product.

Common names have been given to sodium sulfate as a result of manufacturing methods. In rayon production, by-product sodium sulfate is separated from a slurry by filtration where a 7–10-cm cake forms over the filter media. Thus rayon cake was the term coined for this cake. Similarly, salt cake, chrome cake, phenol cake, and other sodium sulfate cakes were named. Historically, sulfate cakes were low purity, but demand for higher purity and controlled particle size has forced manufacturers either to produce higher quality or go out of business.

**1.2. Occurrence.** Minerals of sodium sulfate occur naturally throughout the world. The deposits result from evaporation of inland seas and terminal lakes. Colder climates, such as those found in Canada and the former Soviet Union, favor formation of mirabilite. Warmer climates, such as those found in South America, India, Mexico, and the western United States, favor formation of thenardite. In areas where other anions and cations are present, double salts can be found of the kinds shown in Table 2, which lists nearly all naturally occurring minerals containing sodium sulfate. Except for mirabilite, thenardite, and astrakanite, these mineral deposits play a minor role in sodium sulfate production.

**1.3. Physical and Chemical Properties.** Physical and chemical properties of the three most important forms of sodium sulfate are summarized in Table 3. The solubility of sodium sulfate in water from 0 to 360°C is shown in Figure 1 (2). The solubility of the $NaCl{\cdot}Na_2SO_4{\cdot}H_2O$-saturated system is also shown. The aqueous solubility of sodium sulfate changes rapidly from 0 to 40°C, and addition of NaCl to a saturated solution of $Na_2SO_4$ dramatically suppresses this solubility. These two effects are exploited by all manufacturers of sodium sulfate.

The reactivity of $Na_2SO_4$ is relatively low at room temperature with the exception of sulfuric acid, with which various other acid compounds are formed at temperatures below 100°C. At higher temperatures $Na_2SO_4$ is very reactive (3).

Sodium sulfate decahydrate melts incongruently at 32.4°C to a sulfate liquid phase and an anhydrous sulfate solid phase. The presence of other salts, such as NaCl, can depress the melting point to 17.9°C.

Sodium sulfate crystallized from solution has an attraction for iron and iron compounds and for various organics. Glauber's salt does not show this attraction and in fact rejects most impurities. Thus higher quality $Na_2SO_4$ is made from Glauber's salt.

### 1.4. Manufacture and Processing.

Nearly all manufacturers of sodium sulfate use Glauber's salt in an intermediate process step. Glauber's salt is then converted to anhydrous sodium sulfate. In 2004, there were only two significant producers of natural sodium sulfate: Cooper Natural Resources (Texas) and Searles Valley Minerals (California).

In Texas, subterranean sulfate brines are pumped to the surface where the brines are first saturated with NaCl before they are cooled by mechanical refrigeration to form Glauber's salt (4,5). This salt is then separated from its mother liquor, melted, and dehydrated with mechanical vapor recompression evaporators (6).

Processing at Searles Lake, California, is similar to that of Texas brines. Brine is cooled to 16°C to remove borax crystals, then cooled to 4°C which precipitates Glauber's salt. This salt is then separated from its mother liquor, melted in multi-effect vacuum crystallizers to form anhydrous sodium sulfate, and dried. Both processes produce crystals that are 99.3–99.7% pure (6).

Formerly, at Great Salt Lake Minerals Corporation (Utah), solar-evaporated brines are winter-chilled to −3°C in solar ponds. At this low temperature, a relatively pure Glauber's salt precipitates. Ponds are drained and the salt is loaded into trucks and hauled to a processing plant. At the plant, Glauber's salt is dissolved in hot water. The resulting liquor is filtered to remove insolubles. The filtrate is then combined with solid-phase sodium chloride, which precipitates anhydrous sodium sulfate of 99.5–99.7% purity. Great Salt Lake Minerals Corporation discontinued sodium sulfate production in 1993.

Figure 2 shows a general process flow diagram for almost all production of natural sodium sulfate. Glauber's salt can be converted to anhydrous sodium sulfate by simply drying it in rotary kilns. Direct drying forms a fine, undesirable powder, and any impurities in the Glauber's salt become part of the final product. This process is not used in the United States but is used in other countries.

The Mannheim process produces sodium sulfate by reaction of sodium chloride and sulfuric acid.

$$NaCl + H_2SO_4 \rightarrow Na_2SO_4 + HCl$$

This reaction takes place in a fluidized-bed reactor or a specially made furnace called a Mannheim furnace. This method was last used in the United States in the 1980s. In another process, $SO_2$, $O_2$, and $H_2O$ react with NaCl.

$$4\ NaCl + 2\ SO_2 + O_2 + 2\ H_2O \rightarrow 2\ Na_2SO_4 + 4\ HCl$$

This is called the Hargreavesprocess. Only a minor amount of sodium sulfate is made in the United States using the Hargreaves process, but both the Hargreaves and the Mannheim processes are used widely in the rest of the world. Table 4 lists North American producers and capacity information for natural and synthetic sulfate in 2004.

### 1.5. Economic Aspects.

The majority of uses of sodium sulfate have shown flat or negative growth. Powdered home laundry detergents may contain about 50% sodium sulfate, but the market for liquid detergent, which does not contain sodium sulfate, continues to grow. Sodium sulfate consumption in the textile industry has also been declining because of imports taking over the U.S. market. However, growth in the powdered laundry detergents outside the U.S. (approximately 80% of world sulfate use is for detergents) and the expanding textile sectors in Central America and South America may result in increased U.S. sodium sulfates exports. World production and consumption of sodium sulfate have been stagnant, but are expected to grow in the next few years, especially in Asia and South America (1).

Table 5 lists some important U.S. statistics for sodium sulfate.

### 1.6. Specifications, Standards, and Quality Control.

Specifications vary with use. The paper and detergent industries are concerned with whiteness and specify various methods to describe color and black or dark specks. It is also important in the detergent industry that sodium sulfate has a particle size and density compatible with other components in the blend to eliminate segregation when it is handled. A typical specification for detergent-grade sodium sulfate is given in Table 6.

Moisture content must be held at low levels or bulk material hardens or cakes. Material that cakes causes severe handling problems anywhere it is stored and reclaimed.

Components of sodium sulfates are easy to analyze using standard procedures. Except for normal analytical care in handling samples, no special precautions or procedures are required.

### 1.7. Health and Safety.

Environmental concerns have influenced $Na_2SO_4$ manufacturing. For example, whereas waste $Na_2SO_4$ was historically discharged into waterways, regulations prohibit discharges of liquids containing sulfate into the environment. This affects paper producers as well as by-product producers. In general, $Na_2SO_4$ is not considered an environmentally dangerous material, but the Mannheim and Hargreaves processes are practically nonexistent in the United States because it is difficult to keep emissions of particulate $Na_2SO_4$ low and keep HCl from escaping to the atmosphere.

Sodium sulfate in moderation is used as a diuretic and cathartic for humans and animals (9) (see Gastrointestinal agents). It is also used in consumer products such as laxatives, antacids, and as a natural filler it is used extensively in powdered laundry detergents (see Detergency).

It is moderately toxic by intravenous route and mildly toxic by ingestion (10).

Sodium bisulfate, $NaHSO_4$, is mildly acidic. Appropriate precautions should be taken when using it.

### 1.8. Uses.

The principal uses of $Na_2SO_4$ are in the manufacture of paper, soaps, and detergents. The kraft paper process uses a mixture of sodium sulfide and sodium hydroxide to digest wood chips. Both the sulfide and hydroxide are generated, starting with sodium sulfate as the raw material.

At low temperatures, $Na_2SO_4$ is nonreactive; because of this and given its relatively low cost, it is used as a filler in household soaps and detergents. Detergents average about 20% $Na_2SO_4$, but some grades have much higher content. Besides adding bulk to the detergent, particle size and whiteness of the sulfate improve appearance, handling characteristics, and assist the detergent in its ability to clean.

Properties of sodium sulfate help speed up the melting process in glassmaking. Its use reduces the tendency for alkaline gas bubbles to form in the glass and provides a less expensive form of $Na_2O$ than soda ash (6). Sodium sulfate improves the working properties of high silica glasses.

Both $Na_2SO_4$ and $NaHSO_4$ are used to adjust pH and dilute dyes. Sodium sulfate is used in cattle feed (see Feeds and feed additives), in cellulose-sponge, as a cement and plaster hardener, and as an aid in metallurgy refining. Glauber's salt, $Na_2SO_4 \cdot 10H_2O$, has a high heat of crystallization. This fact together with its low cost have made it a candidate as a means of storing solar energy (qv). When heated, it melts, absorbing large quantities of heat. When cooled, it recrystallizes, releasing its heat (11,12). Researchers are working to develop ways to use it as an effective energy-storing salt.

Sodium bisulfate, $NaHSO_4$, is a convenient mild acid and is safe for uses as a household toilet-bowl cleaner, automobile-radiator cleaner, and for swimming pool pH adjustment. It is used for metal pickling, as a dye-reducing agent, for soil disinfecting, and as a promoter in hardening certain types of cement.

## 2. Sodium Sulfides

### 2.1. Sodium Hydrosulfide

*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 (13).

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) (14). In aqueous solution NaHS has an alkaline pH. Boiling points, densities, and freezing points for solutions of varying strengths are shown in Figure 3 (13). When exposed to air, sodium hydrosulfide undergoes autoxidation and gradually forms polysulfur, thiosulfate, and sulfate. It also absorbs carbon dioxide, forming sodium carbonate.

*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.

$$H_2S + NaOH \rightarrow NaHS + H_2O$$

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.

*Economic Aspects and Uses.* Uses of NaHS in the United States for 2003 are as shown in Table 7.

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 (16) (see Engineering plastics; Polymers containing sulfur).

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:

$$NaHS + NaOH \rightarrow Na_2S + H_2O$$

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 (17). Sulfide application offers several advantages over the conventional hydroxide processes. The lower solubility of sulfide metals provides improved metal removal efficiency (Fig. 4). 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 (20).

Western Europe demand for sodium hydrosulfide is expected to remain stable for the next five years because of stable leather tanning consumption. Capacities in Europe have remained the same despite tanning activities shutting down due to environmental concerns and investments made to meet these concerns.

In Japan, sodium hydrosulfide is consumed mainly for the production of chemicals and dyes, in wastewater treatments, and leather tanning. A major use has been in the production of polyphenylene sulfide resins. Demand for sodium hydrosulfide is expected to remain unchanged for the next five years (21).

### 2.2. Sodium Sulfide

*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 5 shows the boiling points, densities, and freezing points for various solution strengths (13). 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) (22). 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 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.

*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.

$$Na_2SO_4 + 4\ C \rightarrow Na_2S + 4\ CO$$

$$Na_2SO_4 + 4\ CO \rightarrow Na_2S + 4\ CO_2$$

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.

$$BaS + Na_2CO_3 \rightarrow BaCO_3 + Na_2S$$

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.

*Economic Aspects and Uses.* In the United States, sodium sulfide is used mainly in the leather industry for dehairing leather before tanning and is similar to sodium hydrosulfide in this and other applications. The leather industry has been declining steadily as operations move outside the United States. This trend is expected to continue.

In Western Europe, sodium sulfide is consumed mainly in leather tanning. Use in textile and paper dyeing with sulfur dyes has drastically decreased with the switch from sodium sulfide to glucose. A major worldwide use of sodium sulfide has been the production of polyphenylene sulfide (PPS) resins; however, PPS is no longer produced in Western Europe. Western European demand for sodium sulfide is expected to remain stable over the next five years, with decreasing use in chemicals and dyes being balanced by an increase in leather processing.

In Japan, sodium sulfide is consumed mainly in the production of chemicals and dyes, in wastewater treatment and in leather tanning. A major use of sodium sulfide has been the production of polyphenylene sulfide (PPS) resins. Japanese demand for sodium sulfide is expected to remain unchanged over the next years (21).

**2.3. 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.

**2.4. 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 (13).

**2.5. Health and Safety Factors.** 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 (23).

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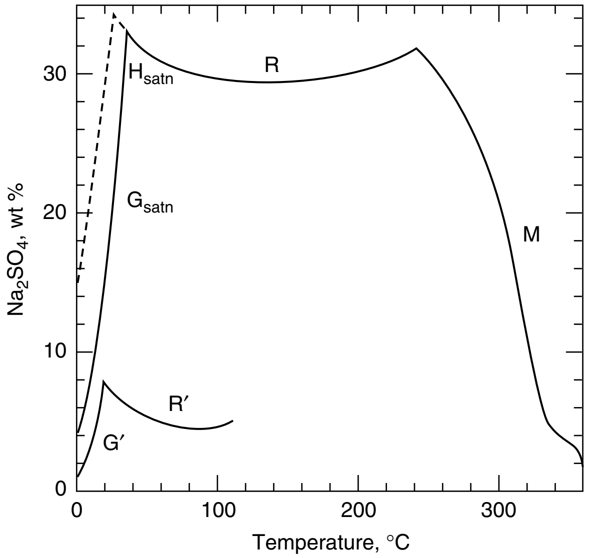

**Fig. 1.** Solubility system of (—) $Na_2SO_4{\cdot}H_2O$ where R and M refer to rhombic and monoclinic $Na_2SO_4$, respectively, in $H_2O$; $G_{satn}$ and $H_{satn}$ represent Glauber's salt and sodium sulfate hemihydrate, $Na_2SO_4{\cdot}7H_2O$, respectively, at saturation in $H_2O$; and (—) $Na_2SO_4{\cdot}NaCl{\cdot}H_2O$ where R′ and G′ represent the rhombic form and Glauber's salt, both saturated with NaCl. The dashed line represents a metastable form.

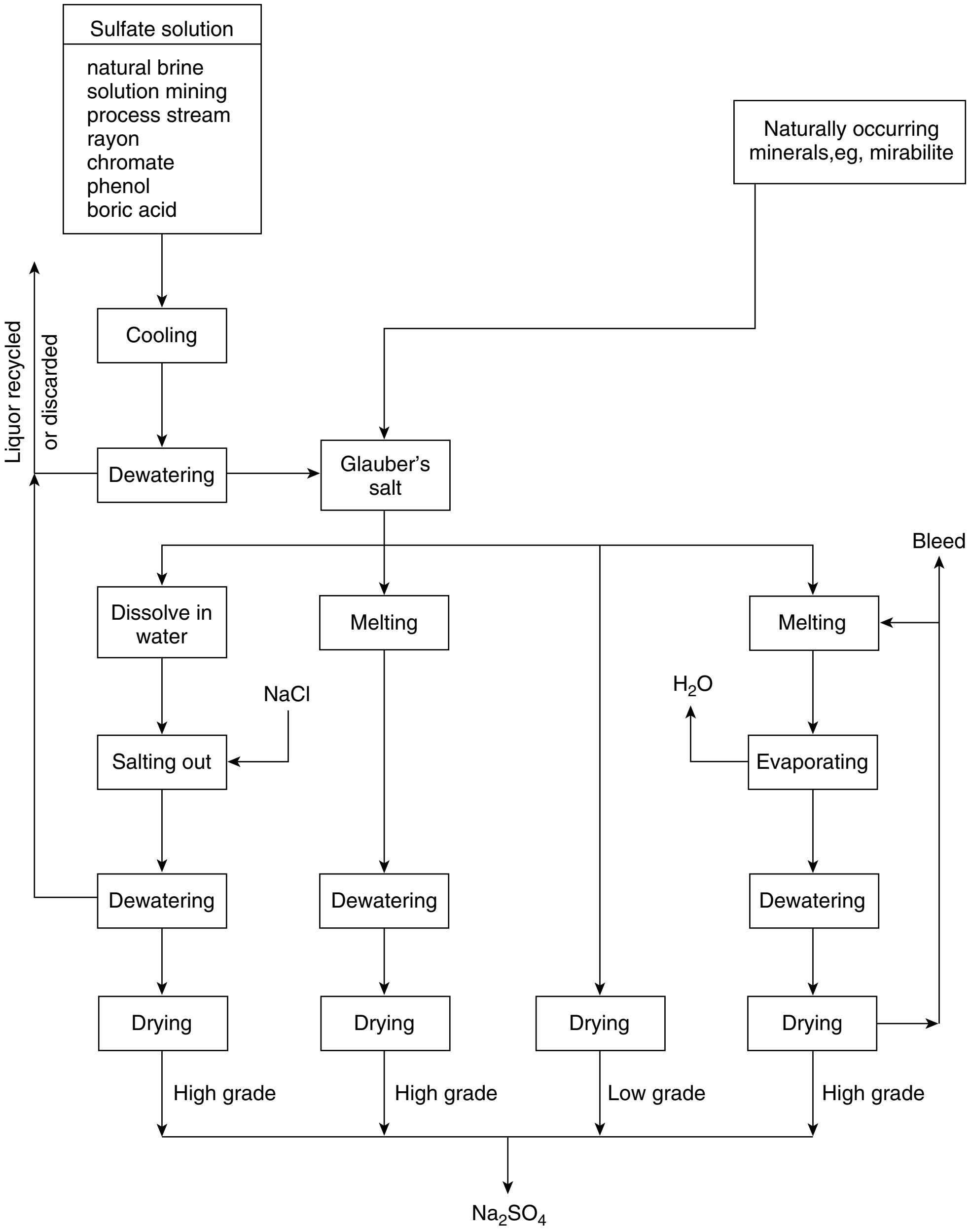

**Fig. 2.** Natural $Na_2SO_4$ processing methods.

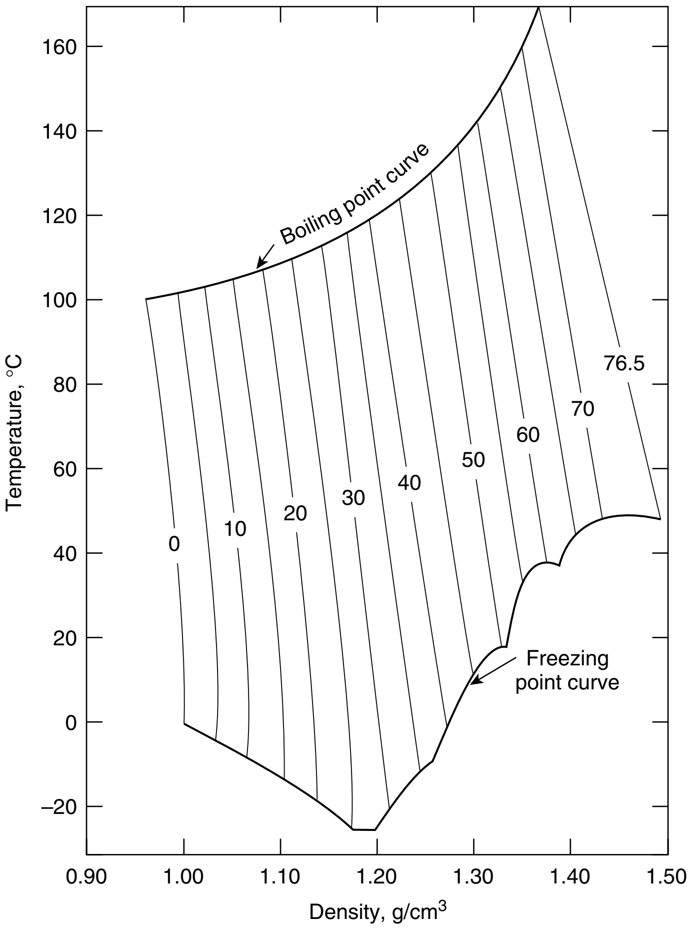

**Fig. 3.** Density of sodium hydrosulfide solutions in water, where the numbers on the vertical lines represent concentrations of NaSH in wt % (13).

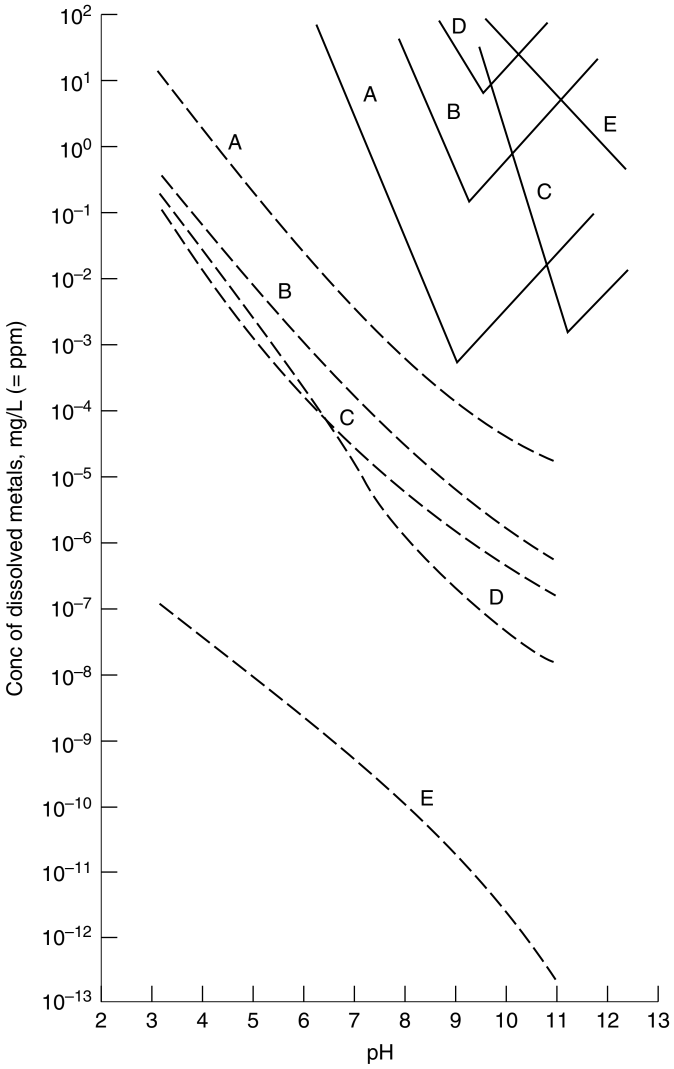

**Fig. 4.** Solubilities of (—) metal hydroxides, $M(OH)_2$, and (– – –) metal sulfides, MS, as a function of pH, where A–D correspond to M = Cu, Zn, Cd, and Pb, respectively (18). For E, the formulas are (—) AgOH and (– – –) $Ag_2S$. Curves for metal sulfides are based on experimental data listed in Reference 19.

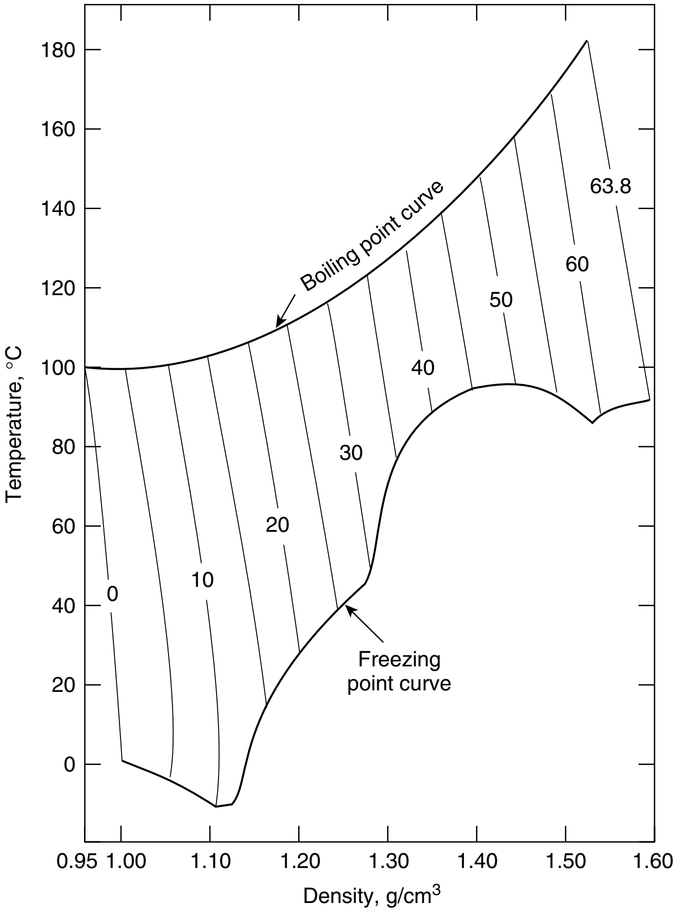

**Fig. 5.** Density of sodium sulfide solutions in water, where the numbers on the vertical lines represent concentrations of $Na_2S$ in wt % (13).

Table 1. **Sulfates of Sodium**

| Chemical name | CAS Registry Number | Mineral name | Common name | Formula |
|---|---|---|---|---|
| sodium sulfate | [7757-82-6] | thenardite | salt cake[a] | $Na_2SO_4$ |
| sodium sulfate decahydrate | [7727-73-3] | mirabilite | Glauber's salt | $Na_2SO_4 \cdot 10H_2O$ |
| sodium bisulfate | [7681-38-1] | | niter cake | $NaHSO_4$ |

[a] Whereas at one time the name salt cake implied a low grade material, increasingly it is used as another name for both high and low grade $Na_2SO_4$.

Table 2. **Minerals Containing Sodium Sulfate**

| Mineral name | Composition |
|---|---|
| aphthitalite (glaserite) | $Na_2SO_4 \cdot 3K_2SO_4$ |
| astrakanite (bloedite) | $Na_2SO_4 \cdot MgSO_4 \cdot 4H_2O$ |
| burkeite | $2Na_2SO_4 \cdot Na_2CO_3$ |
| d'ansite | $9Na_2SO_4 \cdot MgSO_4 \cdot 3NaCl$ |
| ferrinatrite | $3Na_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 6H_2O$ |
| glauberite | $Na_2SO_4 \cdot CaSO_4$ |
| Glauber's salt (mirabilite) | $Na_2SO_4 \cdot 10H_2O$ |
| hanksite | $9Na_2SO_4 \cdot 2Na_2CO_3 \cdot KCl$ |
| hydro-glauberite | $5Na_2SO_4 \cdot 3CaSO_4 \cdot 6H_2O$ |
| loweite | $Na_2SO_4 \cdot MgSO_4 2.5H_2O$ |
| thenardite | $Na_2SO_4$ |
| tychite | $Na_2SO_4 \cdot 2Na_2CO_3 \cdot 2MgCO_3$ |
| vanthoffite | $3Na_2SO_4 \cdot MgSO_4$ |

Table 3. **Properties of Sodium Sulfates**

| | Sodium sulfate | | |
|---|---|---|---|
| Property | Anhydrous | Decahydrate | Sodium hydrogen sulfate |
| mol wt | 142.05 | 322.21 | 120.06 |
| mp, °C | 884 | 32.4 | 315 |
| specific gravity | 2.664 | 1.464 | 2.435 |
| specific heat, J/(gK)[a] | 0.845 | | |
| heat of formation, kJ/mol[a] | −1385 | −4322 | −1125 |
| heat of solution, kJ/mol[a] | 1.17 | −78.41 | 7.28 |
| heat of crystallization, kJ/mol[a] | −8.8 | 78.2 | |
| refractive index | 1.464 | 1.394 | 1.459 |
| crystalline form | rhombic, monoclinic, and hexagonal | monoclinic | triclinic |

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

Table 4. **North American Producers and Production Capacity of Sodium Sulfate**[a]

| Producer | Location[b] | Capacity × $10^3$ t |
|---|---|---|
| Cooper Natural Resources | Seagraves, Tex. | 131.5 |
| Doe Run | Boss, Mo. | 13.6 |
| DSM | Belvidere N.J. | 22.7 |
| Elementis | Castle Hayne, N.C. | 113.4 |
| Exide Technologies | Baton Rouge, La. | 13.6 |
| Exide Technologies | Frisco, Tex. | 13.6 |
| Indspec | Petrolia, Pa. | 36.3 |
| J.M. Hubber | Etowah, Tenn. | 31.7 |
| J. M. Huber | Havre de Grace, Md. | 18.1 |
| Liberty Fibers | Lowland, Tenn. | 36.3 |
| Revere Smelting & Refining | Middletown, N.Y. | 18.1 |
| Searles Valley Minerals, | Westend Calif.[b] | 208.6 |
| other U.S. Producers | | 40.8 |
| Milar Western Industries, | Palo, Saskatchewan, Canada[b] | 99.8 |
| Penoles (Quimica del Rey) | Coahulla, Mexico[b] | 526.2 |
| Saskatchewan Minerals | Chaplin, Saskatchewan, Canada[b] | 113.4 |
| *Total North American* | | *1,438* |

[a] Ref. 7.

[b] From natural sources, others as by-product.

Table 5. **United States Statistics for Sodium Sulfate, ×$10^3$ t**[a, b]

| Category | 2000 | 2001 | 2002 | 2003 | 2004[c] |
|---|---|---|---|---|---|
| production, total (natural and synthetic) | 462 | 512 | 500 | 472 | 425 |
| imports for consumption | 73 | 34 | 51 | 45 | 45 |
| exports | 165 | 191 | 139 | 154 | 140 |
| consumption, apparent (natural and synthetic) | 370 | 355 | 412 | 363 | 330 |
| price, quoted, sodium sulfate (100% $Na_2SO_4$), bulk, f.o.b. works, East, dollars per short ton | 114.00 | 114.00 | 114.00 | 114.00 | 114.00 |
| employment, well and plant, number[c] | 225 | 225 | 225 | 225 | 225 |
| net import reliance[d] as a percentage of apparent consumption | E | E | E | E | E |

[a] Ref. 1.

[b] E = net exporter.

[c] Estimated.

[d] Imports − exports + adjustments for Government and industry stock changes.