Kirk-Othmer Encyclopedia of Chemical Technology.

THIOSULFATES

The thiosulfate ion, $S_2O^{2-}{}_3$, is a structural analogue of the sulfate ion where one oxygen atom is replaced by one sulfur atom. The two sulfur atoms of thiosulfate thus are not equivalent. Indeed, the unique chemistry of the thiosulfate ion is dominated by the sulfide-like sulfur atom which is responsible for both the reducing properties and complexing abilities. The ability of thiosulfates to dissolve silver halides through complex formation is the basis for their commercial application in photography (qv).

1. Physical Properties

1.1. Structure

The thiosulfate sulfur atoms have been shown to be nonequivalent by radioactive sulfur exchange studies (1). When a sulfite is treated with radioactive sulfur and the resulting thiosulfate decomposed to sulfur and sulfite by acids, the radioactivity appears in the sulfur:

$$^{35}S + SO_3^{2-} \xrightarrow{35} SSO_3^{2-}$$

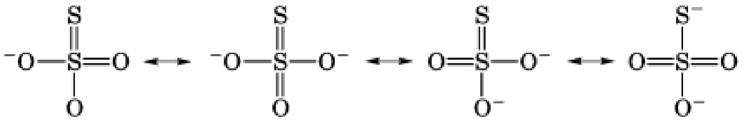
$$^{35}SSO_3^{2-} + H^+ \xrightarrow{35} S + HSO_3^-$$

When the silver salt of the radioactive thiosulfate [83682-20-6] is decomposed, the radioactivity appears in the sulfide:

$$Ag_2^{35}SSO_3 + H_2O \longrightarrow Ag_2^{35}S + H_2SO_4$$

If both sulfur atoms were equivalent, the radioactivity would be equally divided between the two products.

Calculations from binding-force measurements (2) indicate the limiting structural forms of the thiosulfate ion:



(1) (2)

Structure **(1)** explains the formation of sulfur and sulfite in the presence of acid; structure **(2)** is consistent with the formation of sulfide and sulfate in the presence of heavy metals. The bonding in thiosulfate complexes and the chemistry of thiosulfates are normally explained on the basis of **(2)** (see also Sulfur compounds).

The thiosulfate ion has tetrahedral C_{3v} symmetry and the six fundamental modes are both infrared and Raman active. The calculated frequencies (3) are in good agreement with experimental values (4).

Calculated N, cm^{-1}	Experimental N, cm^{-1}
995	1002
669	672
435	451
1123	1125
541	541
335	339

The low value of the S–S force constant compared to that of S–O is consistent with the ease of cleavage of the S–S bond. Spectral data indicate that the structure of the thiosulfate ion in solid thiosulfates is the same as that of the ion in solution.

X-ray crystallographic analysis of the sodium thiosulfate pentahydrate [10102-17-7] crystal indicates a tetrahedral structure for the thiosulfate ion. The S–S bond distance is 197 pm; the S–O bond distance is 148 pm (5). Neutron diffraction of a barium thiosulfate monohydrate [7787-40-8] crystal confirms the tetrahedral structure and bond distances for the thiosulfate ion (6).

1.2. Thermodynamic Properties

The heat of formation of the thiosulfate ion, −5.75 kJ/g (−1.37 kcal/g), was determined by studying the equilibrium of the following reaction:

$$2\,Ag + S_2O^{2-}{}_3 \longrightarrow Ag_2S + SO_3^{2-}$$

and by direct calorimetric experiments (7). The standard free energy of formation is −4.58 kJ/g (−1.09 kcal/g). The partial molal entropy is 62.8 ± 25.1 J/K (15 ± 6 cal/K).

1.3. Electrochemical Properties

The oxidation potential for the reaction

$$2\,S_2O^{2-}{}_3 \rightleftarrows S_4O^{2-}{}_6 + 2\,e^-$$

ranges from 0.2 to 0.4 V in neutral solution, depending on the method of measurement (8). The electrolytic oxidation of thiosulfate solutions yields tetrathionate, $S_4O^{2-}{}_6$, as the principal product; $HSO^{-}{}_3$ is the by-product in acid solutions and $S_3O^{2-}{}_6$ is in alkaline solutions. The electrolytic oxidation is catalyzed by trace amounts of iodide (9).

Electrolytic reduction with a mercury or platinum electrode produces equimolar amounts of sulfide and sulfite:

$$S_2O_3^{2-} + 2\,e \longrightarrow S^2 + SO_3^{2-}$$

2. Chemical Properties

2.1. Thiosulfuric Acid

Thiosulfuric acid [14921-76-7] is relatively unstable and thus cannot be recovered from aqueous solutions. In laboratory preparation, a lead thiosulfate [26265-65-6] solution is treated with H_2S to precipitate PbS, or a concentrated solution of sodium thiosulfate [7772-98-7] is treated with HCl and cooled to $-10°C$ to crystallize NaCl. Aqueous solutions of thiosulfuric acid spontaneously decompose to yield sulfur, SO_2, and polythionic acids, $H_2S_nO_6$. Thiosulfuric acid is a strong acid comparable to sulfuric acid. Dissociation constants, $K_1 = 0.25$, $K_2 = 0.018$, have been determined from pH measurements using a glass electrode (10).

Pure thiosulfuric acid has been prepared in liquid CO_2 at $-50°C$ (11) or in diethyl ether at $-78°C$ (12). It decomposes at $-30°C$ to $H_2S_3O_6$ [27621-39-2] and H_2S, and rapidly at higher temperatures to H_2O, SO_2, and sulfur (13).

2.2. Thiosulfates

The ammonium, alkali metal, and alkaline-earth thiosulfates are soluble in water. Neutral or slightly alkaline solutions containing excess base or the corresponding sulfite are more stable than acid solutions. Thiosulfate solutions of other metal ions can be prepared, but their stability depends on the presence of excess thiosulfate, the formation of complexes, and the prevention of insoluble sulfide precipitates.

Acidification of thiosulfate with strong acid invariably leads to decomposition with the formation of colloidal sulfur and sulfur dioxide. The mechanism of this reaction is complex and depends on the thiosulfate concentration and the pH (14). The following reaction explains the formation of the main products:

$$H^+ + S_2O_3^{2-} \longrightarrow \left[HS_2O^-{}_3\right] \longrightarrow HSO_3^- + S^0 \longrightarrow SO_2 + S^0 + H_2O$$

By-products are also formed:

$$3\ S_2O^{2-}{}_3 + 3\ H^+ \longrightarrow H_2S + S_4O^{2-}{}_6 + HSO_3^-$$

$$S_2O_3^{2-} + H_2O \longrightarrow SO_4^{2-} + H_2S$$

$$5\ S_2O^{2-}{}_3 + 6\ H^+ \longrightarrow 2\ S_5O^{2-}{}_6 + 3\ H_2O$$

In dilute aqueous solution, the following equilibrium is established (15):

$$S_2O_3^{2-} + H^+ \xleftrightarrow{\quad} HSO_3^- + S \qquad K = 0.013 \text{ at } 11°C$$

This equilibrium explains the stabilization of thiosulfate solutions using sulfite or bisulfite as one of the components of acid photographic fixing baths.

The existence of anhydrothiosulfuric acid [83682-21-7] has been proposed to explain the apparent stability of thiosulfate in concentrated hydrochloric acid solution (16):

$$2\ H_2S_2O_3 \leftrightharpoons H_2S_4O_5 + H_2O$$

2.3. Reactions

Catalytic amounts of arsenic, antimony, or tin salts promote the formation of pentathionate (16):

$$S_2O_3^{2-} + H_2AsO_3^{-} \leftrightharpoons HSO_3^{-} + HAsSO_3^{2-}$$

$$S_2O_3^{2-} + 4\ HSO_3^{-} + 2\ H^{+} \leftrightharpoons 2\ S_3O^{2-}{}_6 + 3\ H_2O$$

$$S_3O_6^{2-} + HAsSO_3^{2-} + H^{+} \leftrightharpoons S_4O^{2-}{}_6 + H_2AsO^{-}{}_3$$

$$S_4O_6^{2-} + HAsSO_3^{2-} + H^{+} \leftrightharpoons S_5O^{2-}{}_6 + H_2AsO^{-}{}_3$$

Mild oxidizing agents such as hydrogen peroxide in acid solutions produce tetrathionates and trithionates (17):

$$2\ S_2O^{2-}{}_3 + H_2O_2 \leftrightharpoons S_4O^{2-}{}_6 + 2\ OH^{-}$$

$$3\ S_2O^{2-}{}_3 + 4\ H_2O_2 \leftrightharpoons 2\ S_3O^{2-}{}_6 + 2\ OH^{-} + 3\ H_2O$$

The presence of Fe^{2+} promotes oxidation to the sulfate:

$$S_2O^{2-}{}_3 + 4\ H_2O_2 \leftrightarrows^{Fe^{2-}} 2\ SO_4^{2-} + 2\ H^{+} + 3\ H_2O$$

The reaction with iodine in neutral or slightly acid solution is the basis of a volumetric analytical procedure.

$$2\ S_2O^{2-}{}_3 + I_2 \longrightarrow S_4O_6^{2-} + 2\ I^{-}$$

Stronger oxidizing agents such as chlorine, bromine, permanganate, chromate, or alkaline hydrogen peroxide oxidize thiosulfate quantitatively to sulfate:

$$S_2O_3^{2-} + 2\ OH^{-} + 4\ H_2O_2 \rightleftharpoons 2\ SO_4^{2-} + 5\ H_2O$$

Hypochlorite, hypobromite, and hypoiodite are also strong enough to oxidize thiosulfate to sulfate:

$$S_2O_3^{2-} + 4\ BrO^{-} + 2\ OH^{-} \longrightarrow 2\ SO_4^{2-} + 4\ Br^{-} + H_2O$$

Thiosulfates are reduced to sulfides by metallic copper, zinc, or aluminum:

$$S_2O_3^{2-} + 2\ Cu \longrightarrow Cu_2S + SO_3^{2-}$$

The thiosulfate reaction with cyanide to give thiocyanate is the basis for the use of thiosulfate as an antidote in cyanide poisoning:

$$S_2O_3^{2-} + CN^- \longrightarrow SO_3^{2-} + SCN^-$$

Thiosulfates form complex ions with a number of metal ions by the coordination of more than one thiosulfate ion. The stability constants for the lead thiosulfate complexes $[Pb(S_2O_3)_2]^{2-}$ and $[Pb(S_2O_3)_3]^{4-}$ have been determined (18). Mercury forms a thiosulfate complex [83682-22-3], $K_6[Hg(S_2O_3)_4]$, by reaction of mercuric oxide and potassium thiosulfate [10294-66-3] (19). The stability of the silver complex thiosulfates $[Ag(S_2O_3)_2]^{3-}$ and $[Ag(S_2O_3)_3]^{5-}$ is the basis for the use of thiosulfates to dissolve the residual silver chloride in photographic gelatin coatings. The structure of some thiosulfate complexes has been determined (20).

The addition of thiosulfate to aqueous solutions of silver, lead, and copper precipitates the corresponding thiosulfates, which, on heating, decompose to the sulfides. In this manner, thiosulfate can be used as a reagent for most metals having insoluble sulfides. Details of the reactions of other metals with thiosulfate are available (21).

2.4. Corrosion

Copper-base alloys are seriously corroded by sodium thiosulfate (22) and ammonium thiosulfate [7783-18-8] (23). Corrosion rates exceed $10 kg/(m^2 \cdot yr)$ at 100°C. High silicon cast iron has reasonable corrosion resistance to thiosulfates, with a corrosion rate $< 4.4 kg/(m^2 \cdot yr)$ at 100°C. The preferred material of construction for pumps, piping, reactors, and storage tanks is austenitic stainless steels such as 304, 316, or Alloy 20. The corrosion rate for stainless steels is $< 440 g/(m^2 \cdot yr)$ at 100°C (see also Corrosion and corrosion control).

3. Preparation

Thiosulfates are normally prepared by the reaction of sulfur and sulfite in neutral or alkaline solution:

$$S^0 + SO_3^{2-} \longrightarrow S_2O^{2-}{}_3$$

Polysulfides react similarly:

$$S_x^{2-} + SO_3^{2-} \longrightarrow S_2O^{2-}{}_3 + S_{x-1}^{2-}$$

Sulfides react with sulfur dioxide, sulfite, or bisulfite:

$$2\,S^{2-} + 2\,SO_2 + 2\,HSO_3^- \longrightarrow 3\,S_2O^{2-}{}_3 + H_2O$$

$$2\,S^{2-} + 3\,SO_2 + SO_3^{2-} \longrightarrow 3\,S_2O^{2-}{}_3$$

$$2\,HS^- + 4\,HSO_3^- \longrightarrow 3\,S_2O^{2-}{}_3 + 3\,H_2O$$

These three methods are employed commercially. In addition, decomposition of polythionates in alkaline solution or their reaction with sulfide or sulfite gives thiosulfates:

$$4\ S_4O^2{}_6 + 6\ OH^- \longrightarrow 5\ S_2O^{2-}{}_3 + 2\ S_3O^{2-}{}_6 + 3\ H_2O$$

$$S_3O_6^{2-} + S^{2-} \longrightarrow 2\ S_2O^{2-}{}_3$$

$$S_5O_6^{2-} + SO_3^{2-} \longrightarrow S_2O^{2-}{}_3 + S_4O_6^{2-}$$

The high temperature hydrolysis of sulfur in alkaline solutions also produces thiosulfates:

$$S_8 + 6\ OH^- \longrightarrow 2\ S_3^{2-} + S_2O^{2-}{}_3 + 3\ H_2O$$

4. Sodium Thiosulfate

Sodium thiosulfate, either the anhydrous salt, $Na_2S_2O_3$, or the crystalline pentahydrate, is commonly referred to as hypo or crystal hypo. When a concentrated sodium thiosulfate solution (50–60 wt %) is cooled to $<48^\circ C$, the pentahydrate, containing 63.7% $Na_2S_2O_3$, crystallizes in monoclinic transparent prisms as shown in the equilibrium phase diagram (Fig. 1). The monohydrate [55755-19-6] and the heptahydrate [36989-91-0] are also known.

Although 16 different crystalline modifications have been identified (24, 25), the α-pentahydrate is the stable form below 48°C. Solutions of sodium thiosulfate in the absence of seed crystals can be easily supercooled below their normal crystallization temperatures. The dotted line extension of the dihydrate phase in Figure 1 is an indication that, if supercooling takes place below this line, solutions normally giving the pentahydrate may form the dihydrate [36989-90-9] instead.

Selected physical properties of sodium thiosulfate pentahydrate are shown in Table 1. The crystals are relatively stable, efflorescing in warm, dry air and deliquescing slightly in moist air. They melt in their water of hydration at 48°C and can be completely dehydrated in a vacuum oven at this temperature, or at atmospheric pressure at 105°C. Anhydrous sodium thiosulfate can also be crystallized directly from a 72% solution above 75°C. It decomposes at 233°C:

$$4\ Na_2S_2O_3 \longrightarrow 3\ Na_2SO_4 + Na_2S_5$$

Further heating to 440–500°C gives sodium sulfide and sulfur dioxide (33).

Aqueous sodium thiosulfate solutions are neutral. Under neutral or slightly acidic conditions, decomposition produces sulfite and sulfur. In the presence of air, alkaline solutions decompose to sulfate and sulfide. Dilute solutions can be stabilized by small amounts of sodium sulfite, sodium carbonate, or caustic, and by storage at low temperatures away from air and light. Oxidation is inhibited by HgI_2 (10 ppm), amyl alcohol (1%), chloroform (0.1%), borax (0.05%), or sodium benzoate (0.1%).

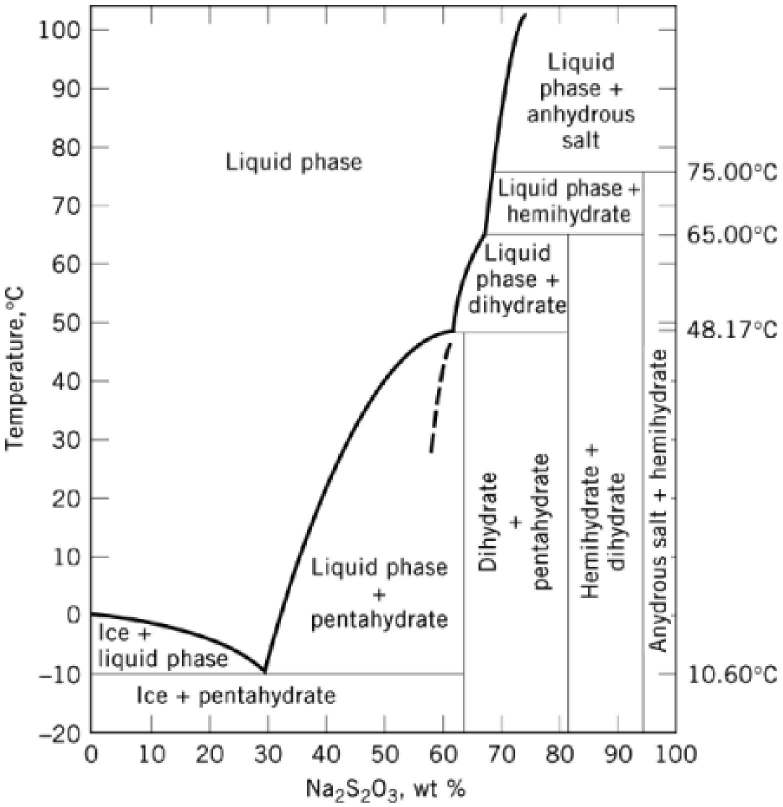


Fig. 1. Equilibrium phase diagram, $Na_2S_2O_3$ and H_2O, where the dashed line is an extension of dihydrate crystal phase (24).

4.1. Manufacture

Sodium thiosulfate has been produced commercially by the air oxidation of sulfides, hydrosulfides, and polysulfides.

Sodium thiosulfate is a by-product of the manufacture of Sulfur Black and other sulfur dyes (qv), where organic nitro compounds are treated with a solution of sodium polysulfide to give thiosulfate. The dyes are insoluble and are recovered by filtration. The filtrate is treated with activated carbon and filtered to obtain a sodium thiosulfate solution. After concentration and crystallization, the final product assays ca 96% $Na_2S_2O_3{\cdot}5H_2O$ (34) (see Dyes and dye intermediates).

Other commercial processes are based on the reaction of sodium sulfide or hydrogen sulfide with sulfur dioxide, and caustic or soda ash:

$$2\ Na_2S + Na_2CO_3 + 4\ SO_2 \longrightarrow 3\ Na_2S_2O_3 + CO_2$$

$$2\ Na_2S + 3\ SO_2 \longrightarrow 2\ Na_2S_2O_3 + S^0$$

Table 1. Physical Properties of Sodium Thiosulfate Pentahydrate

Property	Value	Reference[a]
refractive index, n_D^{20}	1.4886	27
density, d_4^{25}, g/cm^3	1.750	28
heat of solution in water at 25°C, J/g[b]	−187	29
heat of formation, kJ/g[b]	−10.48	30
heat of fusion, J/g[b]	200	31
specific heat J/(g·K)[b]		
solid	1.84	28
molten salt	2.38	28
dissociation pressure, kPa[c]		
20°C	0.796	
25°C	1.154	
30°C	1.679	
35°C	2.395	
vapor pressure of saturated solutions, kPa[c]		28
33°C	1.33	
57°C	5.60	
90°C	31.06	
120°C	100.4	
density of aqueous solutions, d_{20}^{20}, g/cm^3 at wt % $Na_2S_2O_3$		32
1.00	1.0083	
10.00	1.0847	
20.00	1.1760	
30.00	1.2762	
40.00	1.3851	

[a] Ref. 26 gives a comprehensive summary of the properties of sodium thiosulfate and its aqueous solutions.
[b] To convert J to cal, divide by 4.184.
[c] To convert kPa to mm Hg, multiply by 7.5.

Excess sulfur is filtered before evaporation and crystallization. In one modification, excess sulfur is preground in the sodium sulfide solution and an equivalent amount of sodium sulfite added (35).

Another procedure utilizes a slurry of sodium sulfite, produced by the reaction of soda ash with sulfur dioxide, which is digested with excess sulfur until all of the sulfite is used up:

$$Na_2SO_3 + S^0 \longrightarrow Na_2S_2O_3$$

Cationic surface-active agents promote wetting of the sulfur and thereby increase the reaction rate (36). The quality of the product is improved by using photographic-grade sodium sulfite or bisulfite. Excess sulfur is filtered before evaporation (qv) and crystallization (qv). Evaporation is energy-intensive; thus it is important to produce the thiosulfate solution at the highest possible concentration. The purity of the product is typically >99%; sulfite and sulfate are the main impurities.

4.2. Economic Aspects

As of 1995, two manufacturers produced sodium thiosulfate in the United States with an estimated total capacity of 30,000 metric tons. Despite declining volume, prices have increased, reflecting increased raw material, energy, and labor costs. Production outside of the United States is at least 25% of the U.S. production, mainly in Germany.

4.3. Specifications

Sodium thiosulfate pentahydrate and the anhydrous salt are available in various grades, as shown in Tables 2 and 3.

Table 2. Specifications for Sodium Thiosulfate Pentahydrate

Specifications	ACS reagent grade[a]	USP grade[b]
assay, %[c]	99.5	99.0
water, %		32–37
insoluble matter, %[d]	0.005	
sulfate and sulfite, as SO_4, %[d]	0.1	
sulfide, as S, ppm[d]	1	
pH of 5% solution at 25°C	6.0–8.4	
arsenic, ppm[d]		3
heavy metals, ppm[d]		20[e]
nitrogen compounds, as N, %[d]	0.002	

[a] Ref. 37.
[b] Ref. 38.
[c] Value is minimum.
[d] Value is maximum.
[e] Also calcium content must be so as to pass the test.

Table 3. American National Standard Specifications for Photographic-Grade Sodium Thiosulfate[a]

Specifications[b]	Crystalline pentahydrate	Anhydrous
assay, %		
	99.0[c]	97.0[c]
	101.0	
insoluble matter[d], %	0.2	0.4
alkalinity, as NaOH, %	0.02	0.06
acidity, as H_2SO_4, %	0.01	0.01
sulfide, as S, ppm	4	6
heavy metals, as Pb, ppm	10	20
iron, as Fe, ppm	30	50
appearance of solution	to pass test	to pass test

[a] Ref. 39.
[b] Values are maximum unless otherwise noted.
[c] Value is minimum.
[d] Including calcium, magnesium, and ammonium hydroxides, ppt.

4.4. Analytical and Test Methods

An aqueous solution of sodium thiosulfate forms a white precipitate with hydrochloric acid and evolves sulfur dioxide gas which is detected by its characteristic odor. The white precipitate turns yellow, indicating the presence of sulfur. The addition of ferric chloride to sodium thiosulfate solutions produces a dark violet color which quickly disappears.

Sodium thiosulfate is determined by titration with standard iodine solution (37). Sulfate and sulfite are determined together by comparison of the turbidity produced when barium chloride is added after the iodine oxidation with the turbidity produced by a known quantity of sulfate in the same volume of solution. The absence of sulfide is indicated when the addition of alkaline lead acetate produces no color within one minute.

4.5. Health and Safety Factors

The LD_{50} of anhydrous sodium thiosulfate for mice is 7.5 ± 0.752 g/kg (40). Because of low toxicity, it can be safely used in veterinary medicine. Sodium thiosulfate pentahydrate is affirmed as a GRAS indirect and direct human food ingredient under the Federal Food, Drug, and Cosmetic Act (41) (see Food additives).

It has been reported that humans can consume up to 12 g sodium thiosulfate orally per day with no effect other than catharsis (42).

4.6. Uses

The principal use for sodium thiosulfate continues to be as fixative in photography (qv) to dissolve undeveloped silver halide from negatives or prints. In applications where rapid processing is required, such as the processing of x-ray film, sodium thiosulfate has been largely replaced by ammonium thiosulfate.

Sodium thiosulfate is still used in chrome leather tanning as a reducing agent in two-bath processes to reduce dichromate (hexavalent chromium) to chrome alum (trivalent chromium) (see Leather).

In paper (qv) and textiles (qv) manufacture, sodium thiosulfate removes residual bleach before dyeing. It inhibits fermentation in dyeing baths, and is a source of sulfur dioxide in the bleaching of wool. It is also used as a dechlorinating agent for waste streams. Sodium thiosulfate reduces the residual free chlorine in chlorinated potable water to protect the taste of a beverage (43). Both for the dechlorination of potable water and in the various treatments of textiles sodium thiosulfate is a favored dechlorinating agent. The other widely used reducing agents such as sodium metabisulfite and sodium sulfite have pHs of 4.3–4.6 and 9.3–9.5, respectively, whereas the ideal pH for sodium thiosulfate is 7.0–8.0. Using sodium thiosulfate with an inadvertent overdose would not result in the pH being too high or too low.

Minor and potential new uses include flue-gas desulfurization (44, 45), silver-cleaning formulations (46), thermal-energy storage (47), cyanide antidote (48), cement additive (49), aluminum-etching solutions (50), removal of nitrogen dioxide from flue gas (51), concrete-set accelerator (52), stabilizer for acrylamide polymers (53), extreme pressure additives for lubricants (54), multiple-use heating pads (55), in soap and shampoo compositions (56), and as a flame retardant in polycarbonate compositions (57). Moreover, precious metals can be recovered from difficult ores using thiosulfates (58). Use of thiosulfates avoids the environmentally hazardous cyanides.

5. Ammonium Thiosulfate

Ammonium thiosulfate, $(NH_4)_2S_2O_3$, commonly referred to as ammo hypo, has displaced sodium thiosulfate in photography. It is normally sold in the United States only as the aqueous solution. In addition, a crystal slurry and anhydrous crystal are available in Europe.

The anhydrous monoclinic crystalline form has a density of 1.679 g/cm^3 (59); no hydrates are known. Solubility in water is given in Table 4. Ammonium thiosulfate solutions decompose slowly below 50°C and more rapidly at higher temperatures. The anhydrous salt decomposes above 100°C to sulfite and sulfur (60):

$$(NH_4)_2\,S_2O_3 \longrightarrow (NH_4)_2\,SO_3 + S^0$$

At 230–245°C, the ammonium sulfite decomposes.

Table 4. Solubility of Ammonium Thiosulfate

Temperature, °C	$(NH_4)_2S_2O_3$ Solubility, wt %
−30°C	53.5
−20°C	56.5
−10°C	58.5
0°C	60.5
10°C	62.5
20°C	64.0
30°C	65.5
40°C	67.2
50°C	68.5
60°C	69.6
70°C	70.9
80°C	72.2

5.1. Manufacture

Ammonium thiosulfate has been produced by the reaction of ammonium sulfite with sulfur, sulfides, or polysulfides:

$$(NH_4)_2\,SO_3 + (NH_4)_2\,S_8 \longrightarrow (NH_4)_2\,S_2O_3 + (NH_4)_2\,S_7$$

$$(NH_4)_2\,SO_3 + (NH_4)_2\,S_7 \longrightarrow (NH_4)_2\,S_2O_3 + (NH_4)_2\,S_6$$

This reaction series continues until the last polysulfide is ammonium sulfide and the process is completed by reaction with sulfur dioxide:

$$3\ SO_2 + (NH_4)_2\,SO_3 + 2\ (NH_4)_2\,S \longrightarrow 3\ (NH_4)_2\,S_2O_3$$

Ammonium bisulfite can be used in place of the sulfur dioxide. The solution is treated with activated carbon and filtered to remove traces of sulfur. Excess ammonia is added and the solution evaporated if the anhydrous crystalline form is desired. The crystals are dried at low temperature in the presence of ammonia to prevent decomposition (61–63).

Other commercial processes are based on the direct reaction of ammonium sulfite and sulfur (64, 65).

$$(NH_4)_2\,SO_3 + S \longrightarrow (NH_4)_2\,S_2O_3$$

Both batch and continuous processes employ excess sulfur and operate at 85–110°C. Trace amounts of polysulfides produce a yellow color which indicates that all the ammonium sulfite has been consumed. Ammonium bisulfite is added to convert the last polysulfide to thiosulfate and the excess ammonia to ammonium sulfite. Concentrations of at least 70% $(NH_4)_2S_2O_3$ are obtained without evaporation. Excess sulfur is removed by filtration and color is improved with activated carbon treatment or sodium silicate (66). Upon cooling the aqueous concentrated solution, ammonium thiosulfate crystallizes.

Agricultural grades of ammonium thiosulfate are prepared by similar processes and contain some excess sulfur. The sulfur can be removed by washing with carbon disulfide. A typical sulfur-free product contains 87% $(NH_4)_2S_2O_3$, 3.4% $(NH_4)_2SO_3$, and 9.6% $(NH_4)_2SO_4$ (67).

Ammonium thiosulfate, stable as a solution, is produced in the form of a 56–60% solution from ammonia and solid sulfur or an H_2S-rich gas stream or both solid sulfur and H_2S gas streams (68). As a result of availability, only development of solutions for processing x-ray and color film and prints has been encouraged. The evolution of automatic processors to develop and print color reinforced the trend toward use of solutions. Most x-ray laboratories and automatic film and print processors require almost immediate results.

5.2. Specifications

The specifications for photographic-grade ammonium thiosulfate are shown in Table 5. There are no corresponding specifications for the agricultural-grade material.

Table 5. American National Standard Specifications for Photographic-Grade Ammonium Thiosulfate Solution

Specifications[a]	Aqueous solution[b]	Crystalline solid[c]
assay as $(NH_4)_2S_2O_3$, %	56.0–60.0	97.0[d]
insoluble matter[e], %	0.2	0.4
alkalinity, as NH_4OH, %	0.3–1.5	0.4
sulfide, as S, ppm	20	10
sulfite, as SO_3, %	0.70	1.4
heavy metals, as Pb, ppm	10	20
iron, as Fe, ppm	2.5	50
residue after ignition, %	0.1	0.2
specific gravity, at 15/15°C	1.310–1.335	

[a] Values are maximum unless range is given.
[b] Ref. 69.
[c] Ref. 70.
[d] Value is minimum.
[e] Including calcium and magnesium, precipitated by ammonium hydroxide.

5.3. Analytical and Test Methods

Analysis and test methods are similar to those for sodium thiosulfate. Sulfite is determined by an indirect method based on the titration of the acid liberated when both the sulfite and thiosulfate are oxidized with iodine solution (69).

5.4. Health and Safety Factors (Toxicology)

The toxicological properties of ammonium thiosulfate are generally considered to be the same as those of sodium thiosulfate and thiosulfates in general (42).

5.5. Uses

The use distribution of ammonium thiosulfate in 1995 was estimated to be photography, 48%; agricultural applications, 50%; and others, including dechlorination, 2%.

The principal use of photochemical-grade ammonium thiosulfate continues to be in photography, where is dissolves undeveloped silver halides from negatives and prints. It reacts considerably faster than sodium thiosulfate, and the fixing solutions can be used about twice as long as sodium thiosulfate solutions; the washing period to remove residual thiosulfate is shorter.

Agricultural uses for ammonium thiosulfate take advantage of both the sulfur and ammonium content by blending with other nitrogen fertilizers such as urea (71). Some foliar-spray fertilizers contain ammonium thiosulfate together with other metal micronutrients (72, 73). Ammonium thiosulfate or mixtures with ammonium nitrate can also be used as desiccants and defoliants in crop-bearing plants such as cotton (qv), soybean, alfalfa, rice, and peppers (74, 75).

Minor and potential new uses for ammonium thiosulfate include flue-gas desulfurization (76, 77), removal of nitrogen oxides and sulfur dioxide from flue gases (78, 79), converting sulfur in hydrocarbons to a water-soluble form (80), and converting cellulose to hydrocarbons (81, 82) (see Sulfur removal and recovery).

6. Other Thiosulfates

Many other metal thiosulfates, eg, magnesium thiosulfate [10124-53-5] and its hexahydrate [13446-30-5], have been prepared on a laboratory scale, but with the exception of the calcium, barium [35112-53-9], and lead compounds, these are of little commercial or technical interest. Although thallous [13453-46-8], silver, lead, and barium thiosulfates are only slightly soluble, other metal thiosulfates are usually soluble in water. The lead and silver salts are anhydrous; the others usually form more than one hydrate. Aqueous solutions are stable at low temperatures and in the absence of air. The chemical properties are those of thiosulfates and the respective cation.

Thiosulfates are generally prepared by treating aqueous solutions of either calcium or barium thiosulfate with the corresponding carbonate or sulfate of the desired metal. The insoluble calcium or barium sulfates or carbonates are filtered and the thiosulfate recovered from the filtrate by vacuum evaporation.

Other method thiosulfates have been prepared by reaction of suspensions of the metal sulfide with sulfur dioxide. However, these thiosulfates are usually contaminated with polythionates (83).

Some metal thiosulfates are inherently unstable because of the reducing properties of the thiosulfate ion. Ions such as Fe^{3+} and Cu^{2+} tend to be reduced to lower oxidation states, whereas mercury or silver, which form sulfides of low solubility, tend to decompose to the sulfides. The stability of other metal thiosulfates improves in the presence of excess thiosulfate by virtue of complex thiosulfate formation.

The most common form of calcium thiosulfate is the hexahydrate [10035-02-6], $CaS_2O_3{\cdot}6H_2O$, which has triclinic crystals and a density of 1.872 g/cm^3 at 16°C (84). Heating, however, does not give the anhydrous salt because of decomposition at 80°C. At lower temperatures, dehydration stops at the monohydrate [15091-91-5]. The solubility of calcium thiosulfates in water is as follows:

temperature, °C	0	10	20	30	40
CaS_2O_3, wt %	25.8	29.4	33.0	36.6	40.3

Aqueous solutions decompose on heating as low as 60°C with formation of sulfur.

Calcium thiosulfate has been prepared from calcium sulfite and sulfur at 30–40°C, or from boiling lime and sulfur in the presence of sulfur dioxide until a colorless solution is obtained. Alternatively, a concentrated solution of sodium thiosulfate is treated with calcium chloride; the crystalline sodium chloride is removed at low temperature. Concentrated solutions of calcium thiosulfate are prepared from ammonium thiosulfate and lime; the liberated ammonium ion is recycled to the ammonium thiosulfate process (85).

Calcium thiosulfate is not produced commercially in the United States. Uses include fungicide formulations (86), a noncorrosive concrete-set accelerator (87), and a catalyst for polyolefin manufacture (88).

7. Complexes and Organic Thiosulfates

Gold thiosulfate complexes of the form $Na_3[Au(S_2O_3)_2]\cdot 2H_2O$ [19153-98-1] are prepared by addition of gold trichloride to concentrated sodium thiosulfate solution (89). The gold is completely reduced and some thiosulfate is oxidized to tetrathionate. This complex has been used in the treatment of rheumatoid arthritis.

Other complex thiosulfates have been prepared to study crystal properties, eg, cadmium ammonium thiosulfates (90), $NaAgS_2O_3\cdot H_2O$ [37954-66-8] (91), $K_2Mg(S_2O_3)_2\cdot 6H_2O$ [64153-76-0] (92), and $(NH_4)_9[Ag(S_2O_3)_4]Cl_2$ [12040-89-0] (93).

Organic thiosulfate salts are usually prepared by the reaction of alkyl chlorides with sodium thiosulfate:

$$RCl + Na_2S_2O_3 \longrightarrow RSSO_3Na + NaCl$$

Sodium ethyl thiosulfate [26264-37-9] is also known as Bunte's salt after the name of its discoverer. Bunte salts may be thought of as esters of thiosulfuric acid (94–96). In essentially all of their chemical reactions, the cleavage is between the divalent and hexavalent sulfur atom. For example, acid hydrolysis produces a thiol and the acid sulfate:

$$RCH_2SSO_3Na + H_2O \longrightarrow RCH_2SH + NaHSO_4$$

Bunte salts have bacterial, insecticidal, and fungicidal properties, and are also used as chelating agents (qv) or surfactants (qv) (97, 98). Bunte salts have been tested for preirradiation protection for mammals exposed to lethal radiation doses (99, 100) (see Radioprotective agents).

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