

Barium and Barium Compounds

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1. Barium Metal

Barium belongs to group 2 of the periodic table and is one of the alkaline-earth metals. Of the elements barium is 19th in atomic abundance. Its average content in the earth's crust is estimated to be 250 g/t [10].

The soft, silver-colored metal is very reactive and does not occur free in nature. However, its compounds are widely distributed. Its major minerals are barium sulfate (barite, heavy spar) and barium carbonate (witherite). Barium sulfate occurs in large deposits throughout the world, and it is the most important raw material for all other barium chemicals. The total annual world production of barium compounds is estimated around 6×10^6 tons. The total world reserves are thought to be around 450×10^6 tons [11].

DAVY first prepared barium metal by electrolyzing mixtures of barium oxide and mercuric oxide and subsequently evaporating the mercury

in the year 1808 [12]. He proposed the name barium. The principles of the reduction of the oxides of alkaline-earth metals with aluminum were described by MALLETT [13] as early as 1878, but GUNTZ [14] is considered to be the first who obtained a considerable amount of barium of good purity by aluminothermic reduction of the oxide.

1.1. Physical Properties

Barium has a body-centered cubic crystal structure at standard temperature and pressure. It is a soft, silvery white metal of medium specific weight and good electrical conductivity (see Table 1). Ultrahigh-purity barium is described as slightly golden yellow [15]. The color changes into silvery white as soon as the surface is contaminated. It is not easy to obtain samples of ultrahigh purity, and therefore accurate

Table 1. Physical properties of barium

Property	Value
Atomic number Z	56
Relative atomic mass A_r	137.3274
Mass number (natural abundance, %) of stable isotopes	130 (0.106), 132 (0.101), 134 (2.417), 135 (6.592), 136 (7.854), 137 (11.232), 138 (71.698)
Density ρ at 20 °C	3.74 g/cm ³
Melting point mp	726.2 °C
Boiling point bp at 101.3 kPa	1637 °C
Hardness (Mohs scale)	1.25
Crystal structure	body-centered cubic
Lattice constant a_0 at 20 °C	0.5025 nm
Coefficient of linear thermal expansion α_1 (mean, 0–100 °C)	$1.8 \times 10^{-5} \text{ K}^{-1}$
Modulus of elasticity E	$1.265 \times 10^{10} \text{ N/m}^2$
Heat of fusion ΔH_m	7.98 kJ/mol
Heat of vaporization ΔH_v	140.3 kJ/mol
Specific heat capacity c at 20 °C	192 J kg ⁻¹ K ⁻¹
at 900 °C	230 J kg ⁻¹ K ⁻¹
Vapor pressure P at 630 °C	1.33 Pa
730	1.33×10^1 Pa
860	1.33×10^2 Pa
1050	1.33×10^3 Pa
1300	1.33×10^4 Pa
1520	5.33×10^4 Pa
1637	1.013×10^5 Pa
Electrical resistivity ρ Commercial purity	$40 \times 10^{-6} \Omega \text{ cm}$
Extra high purity	$30 \times 10^{-6} \Omega \text{ cm}$
Liquid barium at mp	$314 \times 10^{-6} \Omega \text{ cm}$
Thermal coefficient of electrical resistivity $d\rho/dT$ (mean, 0–100 °C)	$6.5 \times 10^{-3} \text{ K}^{-1}$
Thermal conductivity at 273.2 K	0.185 W/cm K

measurements of some physical properties of barium metal are difficult to carry out. In fact, the values for some physical properties are still the subject of controversy.

1.2. Chemical Properties

Barium is clearly metallic and is strongly electropositive. In all of its compounds it has an oxidation state of +2. Barium is very reactive, and its compounds have high energies of formation. Barium forms stable salts with nearly all oxoacids. Table 2 summarizes the physicochemical properties that are associated with the chemical properties of the element.

Generally speaking, barium is more reactive than magnesium, calcium, or strontium. On heating, it readily combines with the halogens in

Table 2. Physicochemical properties of barium

Property	Value
Work function Φ	$3.38 \times 10^{-19} \text{ J}$ or 2.11 eV
Ionization potential	
First	$8.33 \times 10^{-19} \text{ J}$ or 5.212 eV
Second	$1.60 \times 10^{-18} \text{ J}$ or 10.00 eV
Standard electrode potential	
$\text{Ba}^{2+} + 2 \text{e} \rightarrow \text{Ba}$	– 2.91 V
Electronegativity (Pauling)	0.9
Ionic radius (Ba^{2+} , Pauling)	0.135 nm
Atomic radius	0.217 nm
Enthalpy of hydration (Ba^{2+})	1290 kJ/mol
Standard heats of formation (25 °C)	
BaO	– 558 kJ/mol
BaCl ₂	– 858
BaH ₂	– 191
Ba ₃ N ₂	– 377

strongly exothermic reactions. It also reacts with the chalcogens to form BaO, BaS, BaSe, and BaTe [16]. These compounds are also formed by reduction of the carbonate, sulfate, selenate, or tellurate [17, pp. 917–934]. Barium combines with oxygen even at room temperature. Therefore, the metal must be protected from oxidation by storage under paraffin oil or an inert gas. A series of phosphides can be isolated [18]. Reaction of barium with nitrogen starts at about 250 °C. The compound Ba₃N₂ is formed [17, pp. 917–934], [19].

Silicon reacts with barium at 1150 °C to form the silicides BaSi, BaSi₂, and Ba₃Si₄ [20]. Barium combines with carbon to form the carbide BaC₂ [21]. At moderately elevated temperatures barium reacts with hydrogen to form the hydride BaH₂ [17, pp. 921–922]. Barium reacts vigorously with water, liberating hydrogen, to form the strong base barium hydroxide. The metal reacts similarly with alcohols to form the alkoxides and hydrogen. Barium metal is used for synthesis of barium dipivaloylmethanate as the basic compound for the preparation of high temperature superconducting films by the chemical vapor deposition technique [22]. Barium dissolves readily in liquid ammonia. The blue or black solutions contain amine complexes such as Ba(NH₃)₆. Evaporation of the solvent leaves residues of barium amide, Ba(NH₂)₂, imide, Ba(NH), and nitride, Ba₃N₂ [23, 24].

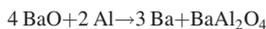
There is an increasing number of organobarium compounds. Alkyl- and arylbarium halogenides, RBaX, as well as dialkyl- and diarylbarium,

R₂Ba, have been synthesized [25, 26]. For a comprehensive review see [27].

Barium forms many alloys, and many binary phases have been described [28]. Nevertheless, only the system barium – aluminum has commercial importance.

1.3. Production

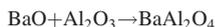
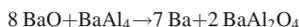
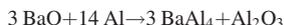
On an industrial scale barium metal is produced in a vacuum by reduction of its oxide with aluminum:



The two-stage process is similar to that for calcium. The raw material is barium oxide (see Section 2.8).

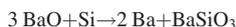
The barium oxide is mixed with aluminum granules, and the mixture briquetted and charged into long tubular retorts of heat-resistant steel. These are evacuated and heated to $\approx 1100^\circ\text{C}$ at the end containing the charge, while the other end is kept cool. Molten aluminum and aluminum vapor react with the solid barium oxide, releasing barium vapor, which condenses in the cooler part of the apparatus [29], where it is collected and cast into chill molds under argon.

BaAl₄ is an intermediate [30], and the net reaction is actually the sum of three reactions:



In the laboratory the aluminothermic reduction of barium oxide is also the most useful method of preparation [7, pp. 920–921], [23, 31–34]. It is also the method of choice for preparing of high-purity samples [35].

Silicon powder can be used to reduce barium oxide, but somewhat higher temperatures are required, 1200°C in a vacuum [36]:



Either no reduction or only partial reduction combined with alloying occurs when barium oxide is treated with magnesium, calcium, sodi-

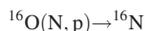
um, or potassium. Barium can be isolated by reaction of barium iodide with sodium, whereas the chloride does not react. Electrolytic methods are not useful for industrial production and are only rarely useful for laboratory synthesis because of the solubility of barium in its molten halides [37]. It is unlikely that barium has ever been isolated in sufficient purity by electrolysis, even though this method has been mentioned numerous times [2].

1.4. Chemical Analysis

Volatile barium compounds impart a pale green color to flames, and this is an effective, simple qualitative test for barium (455.4, 493.4, 553.6, and 611.1 nm).

Barium is separated from magnesium, strontium, and calcium by precipitation from a dilute solution in nitric or hydrochloric acid with a solution of potassium dichromate in aqueous acetic acid. Barium is determined gravimetrically by precipitation of the sulfate [38]; small quantities are determined spectrometrically [39].

The metallic impurities in commercial barium (Table 3) are determined by atomic absorption and flame emission spectroscopy. Trace impurities are best determined by inductively coupled emission spectroscopy (ICP) [41]. The carbon content in barium is determined by combustion; nitrogen, by the Kjeldahl method; and hydrogen, by vacuum hot extraction. Vacuum hot extraction is not useful for analysis of oxygen. Neutron activation analysis based on the reaction



is the recommended method for determination of oxygen in alkaline-earth metals [42].

Table 3. Chemical analysis of commercial barium [40]

Element		Percentage
Ba	(incl. Sr)	99.2 ± 0.30 %
Sr	max.	0.80
Ca	max.	0.25
Al	max.	0.06
C	max.	0.06
Mg	max.	0.02
N	max.	0.02
Fe	max.	0.02
Cl	max.	0.01
Li, Na, K	max.	0.01

1.5. Transportation, Storage, Safety

Barium metal is commercially available in bars up to 20 kg or in rods 22 mm in diameter and 400 mm in length. The rods can be cut into small pieces or extruded into wires.

Barium is packaged in airtight steel drums containing up to 100 kg of the metal under argon or paraffin oil. Smaller amounts (1–10 kg) are packaged in tin cans, and even smaller samples are packaged in hermetically sealed glass bottles [43, 44].

Barium is a flammable solid and cannot be mailed. If it comes into contact with water, there is always the danger of explosion on account of the liberated hydrogen. Therefore barium should always be stored in a dry, well ventilated place and every contact with moisture and air avoided. Protective glasses and safety gloves should be worn while handling barium. Burning barium can be extinguished with sand, aluminum oxide, etc.

Transport classification [40]:

- GGVE, GGVS, RID, ADR: class 4.3, fig. 11b
- IMDG-Code: class 4.3 UN-No. 1400 PG.II
- ICAO: class 4.3 UN-No. 1400 PG.II/Drill-Code 4W

1.6. Uses

The main use of barium and barium – aluminum alloys is as *getter* to remove the last traces of unwanted gases from television picture tubes, transmitter valves, and other vacuum tubes [45–51]. Barium and its aluminum alloys also are used in incandescent lamps [52, 53]. Barium is particularly well suited as a *getter* because it has a low vapor pressure at the working temperatures of the tubes and is very reactive toward undesired gases, such as oxygen, nitrogen, hydrogen, carbon dioxide, water vapor, even removing residues of inert gases by inclusion.

Many other uses of barium have been described in the literature, but they are minor. For example, barium has been used in bearing alloys [54]; in lead – tin soldering alloys, where it increases creep resistance [55]; in nickel alloys for spark plugs [56]; in alloys with calcium, silicon, aluminum, and manganese that are used as deoxidizers for high-grade steel [20, 57]; and as an inoculant for steel and cast iron [58, 59].

Barium has also been used as a modifying agent for silumin, instead of strontium or sodium, because barium also refines the structure of the eutectic aluminum – silicon alloy [60]. Barium is also a good reducing agent; however, it is not normally used for this purpose because of its high atomic mass and its relatively high price, one kilogram of the metal costing about € 130 (\$ 150) in 1998.

1.7. Economic Aspects

The leading producer, Chemetall GmbH, Germany, covers the global demand of Ba and BaAl₄. Nothing is known about production in the GUS and China, although facilities doubtlessly exist.

It is difficult to predict the future demand for barium. However, the replacement of television picture tubes by liquid crystal displays, or similar systems, is likely to decrease demand and production over the long term.

2. Barium Compounds

History. The first mention of barium compounds dates from the year 1602 when V. CASCIOROLUS, in Bologna, realized that barite heated in the presence of organic substances phosphoresces in the dark. Much later, after 1774, C. W. SCHEELE discovered barium oxide and described its properties. He noted that a precipitate formed when sulfuric acid was added to barium oxide dissolved in water.

J. G. GAHN recognized that this was a reaction of the oxide to form barite, i.e., that the oxides were a new class of compounds. At that time the oxide was given the name baryta ($\beta\alpha\rho\upsilon\varsigma$ = heavy), which in some countries is still the name for technical grades: caustic baryta for the oxide, hydrate of baryta for the hydroxide. Today, however, the mineral heavy spar, BaSO₄, is meant by baryta or barite. Barium carbonate also occurs in nature. Native barium carbonate was named witherite, for W. WITHERING discovered the mineral in Cumberland, Great Britain, in 1783.

Raw Materials and Processing. The most important barium mineral is barite (barytes, heavy spar, barium sulfate, BaSO₄), today almost

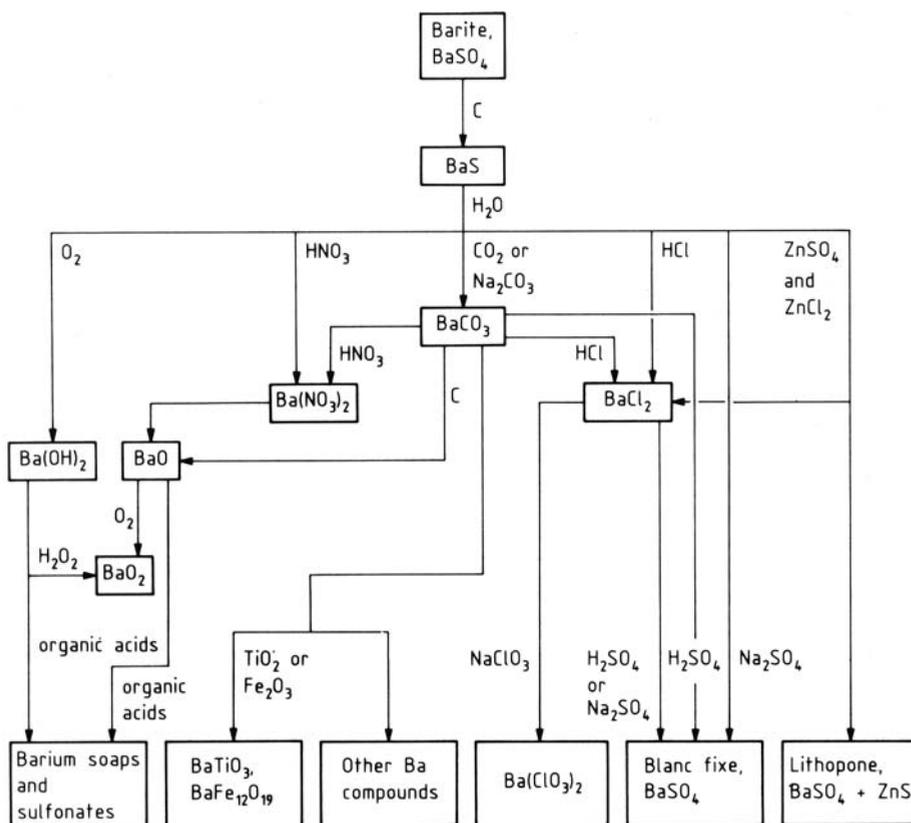


Figure 1. Production pathways to various barium compounds starting from barite

exclusively used as the raw material for the production of barium compounds. Barite occurs all over the earth in hydrothermal vein and sedimentary deposits. The main deposits of the mineral witherite (BaCO_3) are situated in England, Romania, and the USSR, but witherite is no longer of economic importance. No other mineral containing barium is used as a raw material for barium or its compounds at present.

The maximum world output of barite was $\approx 8.3 \times 10^6$ t (1981); however, only 7–8% of this was used for the production of other barium compounds. Figure 1 shows how dressed barite is converted into other barium compounds. The barite is first reduced with carbon to give water-soluble barium sulfide, which is used mainly as an intermediate for the production of all other barium compounds and lithopone [61–65].

Chemical Analysis. All barium compounds may be identified by the green color imparted to flames. For quantitative analysis, atomic absorp-

tion spectroscopy (AAS), flame emission spectroscopy (OES-ICP), X-ray spectroscopy, complexometry, ion chromatography (IC), and gravimetry are suitable. (For chemical analysis of barium metal see Section 1.4.)

Economic Aspects [66, 67]. Production data is available only for barium sulfate, the most important barium compound and the starting material for the production of most other barium compounds. The worldwide barite production has continued to increase from about 5.3×10^6 t in 1996 to 5.8×10^6 t in 2000, 6.5×10^6 t in 2003, 7.3×10^6 t in 2004 up to about 7.6×10^6 t in 2005. Since the 1990s, China has been the main producer of barites and is continuing to strengthen its position. Its share of the market has increased from 30% in 1990 to more than 50% in 2005. Other significant producers are India (14%) and the USA (7%), followed by Morocco (4%), Mexico (4%), and Iran (3%). Barite production primarily reflects worldwide crude oil

and natural gas exploration, since at least about 80 % of its production is used in drilling fluids for these industries. A large portion of this type of barites is used in the oil industry of the Gulf of Mexico. Consumption and the source of barites is mostly dominated by freight costs. In the Gulf of Mexico, for example, most of the barites is imported from China in the form of lumps that are then processed in grinding mills at various locations on the Gulf coast. American sources, mostly from Nevada, are primarily used in Canada and the western and north-western parts of the USA. Indian barite is most competitive in the Middle East and in local markets. Due to the increasing oil demand and the phasing out of Chinese VAT rebates, the prices for barites have continued to rise. Increasing freight rates due to globalization of the markets have assisted in this development. Depending upon the price of the barites, haematite may be a possible replacement, depending upon freight rates. As of today, awareness for environmental issues is growing, such as the mercury contents of the barites used.

The other important uses of barite are as a starting material for the production of barium compounds (see Fig. 1) and its direct use in bleached or unbleached form as a filler in paints and plastics. Consumption of barite in drilling muds varies considerably, while the other two markets are less subject to change. Therefore, it is difficult to obtain reliable relative percentage data. An estimated balance for 1995 is 76–80 % for oil development, 9–13 % for industrial use, and 5–9 % for direct use as a filler.

Identified barite reserves amount to 170×10^6 t with prospects for a total of 500×10^6 t worldwide.

2.2. Barium Sulfate

Barium sulfate is the most important barium compound, and the mineral barite, BaSO_4 , also called heavy spar or barytes, is by far the most important barium mineral.

2.2.1. Properties

Barium sulfate [13462-86-7], BaSO_4 , M_r 233.39. The industrially precipitated product is called blanc fixe [7727-43-7], which is French for “per-

manent white”. Pure BaSO_4 forms colorless rhombic crystals of refractive index ≈ 1.64 , hardness 3–3.5 (Mohs scale), and density ρ 4.48 g/cm^3 . Heating BaSO_4 decomposes it, the rate increasing with temperature over the range 1100–1500 °C. The main products are BaO , SO_2 , and O_2 . For this reason melting points given in the older literature – 1345 °C or 1580 °C – differ. Barium sulfate is almost insoluble in water, the solubility being 2.5×10^{-4} wt % at 20 °C and 3.9×10^{-4} wt % at 100 °C. The solubility of barium sulfate is enhanced by the presence of chelating compounds. For example, it is dissolved by aqueous ethylenediamine tetraacetic acid (EDTA). Barium sulfate is more soluble in hot concentrated sulfuric acid and in melts of alkali-metal salts. The most important reaction of barite is its reduction with carbon to produce barium sulfide.

2.2.2. Barite

In nature, barite [13462-86-7] rarely occurs as a pure white mineral; generally, its color is yellowish, pink, reddish brown, dark gray, or black. The main impurities are quartz, calcium carbonate, iron and manganese oxides, fluorite, strontium sulfate, pyrite, lead glance, zinc blende, and sometimes bituminous substances, the impurities and their amounts depending on the particular deposit. To remove these impurities before the barium sulfate is used industrially, in most cases barite is given a preliminary treatment to increase the BaSO_4 content to 90–97 wt %.

Deposits. Barite deposits are found in all regions of the world. The most important sources in Europe are in Germany, France, Italy, the UK, Belgium, and Spain, with minor amounts coming from Portugal and Greece. Kazakhstan, Bulgaria, Romania, and, to a lesser extent, Georgia, Slovakia, and Poland supply the Central and Eastern European markets.

In the Americas, significant deposits are found in the United States, Canada, Mexico, Brazil, and Argentina.

Morocco is the most important producer in Africa, followed by Algeria and Tunisia.

The largest producer of barite is China (appr. 3.8×10^6 t/a). Other major barite producers in the middle and Far East are India, Iran, and

Turkey, with further amounts coming from Indonesia, North Korea, and Thailand, and lesser amounts from Pakistan, Malaysia, Japan, and Australia.

Mining and Dressing of the Ore. Barite is usually mined in open cuts, only sometimes in open pits or underground galleries. The ore is washed in trommels to remove adherent argillaceous impurities, then crushed in breakers, and classified. The various grain sizes are liberated from the mostly quartz gangue in jigs, thus enriching the barium sulfate. This wet mechanical dressing is adequate for many uses. If there is a high degree of intergrowth of quartz and barite and if the ore contains much iron, lead, or zinc, flotation is required. This produces 98 wt % BaSO₄ [69]. Sometimes barite is a byproduct of the flotation of pyritiferous ores. The flotation agents and the pH depend, among other things, on the impurities present in the crude ore [70]. Generally the barite is wet ground to a grain size of 0.1 mm before flotation. Sodium oleate, tall oil, oleic acid, and alkyl sulfonates and sulfates have been used as collectors. Water glass is the preferred depressant, especially for quartz and iron oxides. Flotation processes to depress the BaSO₄ and float the impurities are confined to a few special cases, e.g., ore rich in fluorite [71].

Another method applicable only to special barite types is based on the tendency of these barites to decrepitate. The broken ore is heated to $\approx 700^\circ\text{C}$ in rotary kilns, the barite crystals bursting while the gangue is unaffected. The decrepitated fines rich in barite are screened off from the gangue. The yield depends above all else on the suitability of the barite for this treatment.

Barite grades with special properties are produced for the various industrial uses.

Drilling Muds. About 80% of the world output of barite is ground and used to increase the density of drilling muds, especially for drilling oil and gas wells. The muds consist of an aqueous clay suspension and additives. The large amount of barite that can be added to this suspension allows adjustment of the density to a high value without the viscosity being affected significantly. The increased density allows faster discharge of cuttings and prevents blowouts. The

standards for drilling-mud-grade barite vary from country to country; however, the OCMA or API standards widely accepted [72]. These regulate the viscosities of aqueous suspensions, the density of the barite (related to the barium sulfate content), its particle size distribution, and the content of water-soluble materials. Higher contents of water-soluble materials, especially divalent cations such as calcium, can cause flocculation of the clay components of drilling muds [73].

For the production of barite for drilling muds, generally it is sufficient to jig the ore to increase the density by removing the quartz. In most cases the other impurities do not cause trouble. On the other hand, barite that has been floated must be heated or treated in some other way to destroy its hydrophobic character.

Raw Material for Barium Chemicals. The 7–8% of the total barite production used as a raw material for other barium compounds is always reduced to barium sulfide as the first stage. The BaSO₄ content must be ≥ 95 wt %, and the BaSO₄ should contain as little silica and iron as possible, as these impurities reduce the yield of water-soluble barium sulfide [21109-95-5]. Fluorspar (fluorite) and lead glance interfere with the reduction. Such barite is generally shipped in bulk as coarsely broken material, either granular (jigged) or ground (floated).

Mined Barites [66]. Mined barites may be separated into “white” and “off-white” grades. The whiteness of a barite is a measure for its purity. Off-white grades are used as a source for barium chemicals and directly as off-white fillers.

Off-white Barite Filler. The use of off-white barites is more or less limited to sound-deadening applications and to dark formulations, such as automobile underbody sealants. The sound-deadening action is related to the high density of barium sulfate.

White Ground Barite Filler. Ground barite is used as a filler owing to its resistance to chemicals and weathering, its wettability and dispersibility, and its low adsorption of binders. The properties of barite flour vary, depending on the commercial grade:

Grain size	0.1–40 μm
Brightness (reference, BaSO_4 white standard = 100)	85–95
Refractive index n_D	≈ 1.64
Oil requirement	10–12 g of oil/100 g
Bulk density, tamped	1.4–2.2 g/cm^3
Density	4.0–4.25 g/cm^3

Some white barite grades may be ground directly without further treatment. More usual, however, is to subject the spar to coarse crushing and gravity dressing. Then the granular material is treated in bleaching vats with hot dilute acid, preferably sulfuric or hydrochloric acid, to remove the colored iron or manganese oxides, washed, and dried. The bleached spar is dry-milled in edge or ball mills to obtain the desired grain size, then air classified.

There is a more economical procedure: the coarsely crushed, gravity dressed barite is ground to the desired grain size by continuous wet milling in lined ceramic tubes. The screened suspension of ground material is bleached in agitator vessels, with dilute sulfuric or hydrochloric acid along with reducing agents (e.g., sodium sulfite) or oxidizing agents (e.g., nitric acid), depending on the kind of impurities, then washed, decanted, and dried. If floated barite is used in this process, then the barite must be floated again after bleaching to remove the decomposed organic material [74].

A third bleaching procedure lacks economic importance: here the barite is heated in a rotary kiln by adding alkali-metal salts, e.g., sodium chloride or sodium hydrogensulfate. This procedure is confined to special cases due to its high cost.

The specifications for ground barite are given in DIN 55911 for the Federal Republic of Germany and ISO 3262 internationally. The requirements of the buyers differ in regard to grain size and whiteness. Some products, such as EWO-Albaryt grades of the Deutsche Baryt-Industrie, Bad Lauterberg/Harz, are equivalent to synthetic blanc fixe in many respects. White ground barite is generally shipped in 25 or 50 kg paper bags, 1000 kg big bags, or in silo trucks.

Barite flours are mainly used as fillers and extenders in paints, varnishes, plastics, rubber, linoleum, sealing compounds, stoppers, plasters, and adhesives (5–9% of the total barite production). High-quality grades can be used as an X-ray-opaque medium in medicine, provided they

meet the requirements of the individual countries as given in USP, EP, JP, DAB, etc.

2.2.3. Blanc Fixe

Precipitated barium sulfate is usually called blanc fixe [7727-43-7]. It is mainly used as a filler and extender, in some fields also as a white pigment. The most important properties for the consumer are its insolubility in water and organic binders, its high degree of whiteness, and its homogeneous granulation:

Grain size	0.1–20 μm
Average grain size	0.2–4 μm
Brightness (reference, BaSO_4 white standard = 100)	95–99
Refractive index n_D	≈ 1.65
Oil requirement	12–22 g of oil/100 g
Bulk density, tamped	0.9–2.2 g/cm^3
Density	4.0–4.4 g/cm^3

Certified ultrahigh-purity blanc fixe, which must also fulfill certain handling requirements, is used as a white standard in UV – Vis spectroscopy instead of magnesium oxide, which is no longer user for this purpose.

Production. Blanc fixe is usually precipitated in stirred tanks from solutions of barium chloride or barium sulfide by adding dilute sulfuric acid or sodium sulfate solutions. The sulfuric acid or the sodium sulfate solution must be free from heavy metals that can impart color to the product.

The method of manufacture and the reaction conditions depend on the ultimate use of the blanc fixe, especially the desired grain size. For example, fine-grained blanc fixe is produced by rapid precipitation from highly concentrated solutions at high pH and low temperatures. Coarse blanc fixe is produced from dilute solutions at high temperatures, say 80–100 °C. The use of seed crystals and prolonged residence time, e.g., by stirring for an extended period at low pH, produces a larger average grain size in the finished product. The precipitated blanc fixe is filtered or centrifuged and washed. It is drawn off and packed as paste, slurry, or powder, the last involving an additional process step of drying and perhaps one of regrinding.

A special problem in preparing blanc fixe from barium sulfide and sodium sulfate solutions is washing out the sodium sulfide. However, this problem can be overcome by enlarging the particle size of the extremely fine material by sintering (at 300–1000 °C) with fluxes like sodium sulfate and extracting the clinker [75].

Another procedure for the manufacture of blanc fixe is based on the conversion of an aqueous suspension of barium carbonate with dilute sulfuric acid, sometimes in the presence of small amounts of hydrochloric acid. The resulting product is characterized by its whiteness [76].

Formerly blanc fixe was obtained as a byproduct of hydrogen peroxide production by reaction of barium peroxide and sulfuric acid, but today hydrogen peroxide is prepared by the anthraquinone process (see → Hydrogen Peroxide).

Quality Specifications. In the Federal Republic of Germany, the standards for blanc fixe, the methods of analysis, and tests are defined in DIN 55 911. The various grades differ mainly in grain size. The smaller the grain diameter the higher the luster. In fact, grades are still sometimes characterized as mat, semimat, or lustrous.

The standards for blanc fixe to be used as X-ray-opaque medium in medicine are described and defined for the various countries in USP, EP, JP, DAB, etc. The standards deviate slightly from one to another.

Shipping and Packing. Blanc fixe is shipped as powder (usually in 25 kg paper bags, big bags, or in silo trucks); slurry (30–40 % water in tank trucks); and agglomerate-free paste (25–35 % water in 50 kg polyethylene-lined sacks). Because blanc fixe is nontoxic, it is not classified as a dangerous good.

Uses. About 70 % of the blanc fixe consumed in Western Europe is used in paint and varnish as well as in printing ink as a filler. It is used as a coating pigment to upgrade the surface of paper and is sometimes used as a pulp filler. Photographic paper requires grades free from sulfur and heavy metals, but this market has lost significance. Today, anatase-grade TiO₂ is used instead. Blanc fixe is also used as a filler in plastics, rubber, and adhesives and as an additive in the negative plates of lead storage batteries.

Special grades are used as a medium opaque to X-rays for medical purposes (stomach X-rays).

Nanoscaled barium sulfates have proven useful in improving mechanical properties of certain polymers such as epoxy systems. Similar to nanoscaled titanium dioxides, they are able to improve the hardness as well as the fracture toughness of these polymers [77]. Because of the low refractive index of barium sulfate, it is possible to formulate clear coats with a high transparency even with large amounts of the nanoparticles. These films have an enhanced resistance to chemicals and improved scratch resistance.

2.3. Barium Sulfide and Polysulfides

The principal intermediate between barium sulfate and other barium compounds is barium sulfide.

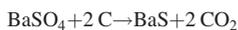
Properties. Pure barium sulfide [21109-95-5], BaS, *M_r* 169.40, *ρ* 4.3 g/cm³, forms colorless cubic crystals. It melts above 1200 °C. Its heat capacity *c_p* is 287 J kg⁻¹ K⁻¹. At room temperature barium sulfide is unaffected by dry air, but over the range 500–1000 °C it is oxidized to barium sulfate, at an ever-increasing rate. In humid air containing carbon dioxide, some barium carbonate forms, and the odor of hydrogen sulfide is noticeable. The solubility of barium sulfide in water depends strongly on the temperature, the maximum being near 90 °C:

°C	0	20	40	60	80	90	100
wt % BaS	2.8	7.3	13.0	21.7	33.3	40.2	37.6

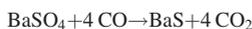
Owing to complete hydrolysis, a solution of sulfide is actually an equimolar solution of barium hydroxide [17194-00-2], Ba(OH)₂, and barium hydrosulfide [25417-81-6], Ba(SH)₂. Accordingly, barium sulfide does not precipitate when the solution is cooled; instead, a double salt of composition Ba(OH)₂ · Ba(SH)₂ · 10 H₂O [42821-46-5] precipitates. Excess hydrogen sulfide converts the barium hydroxide in solution quantitatively to barium hydrosulfide, which can be precipitated as Ba(SH)₂ · 4 H₂O [12230-74-9] by addition of ethyl alcohol.

Aqueous barium sulfide reacts with carbon dioxide to form barium carbonate [513-77-9], BaCO_3 , and the solution is also susceptible to atmospheric oxygen, which easily oxidizes the hydrosulfide to polysulfide, thiosulfate, and sulfite.

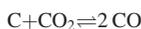
Production. Barium sulfide is produced by reducing barite (BaSO_4) with carbon. The net reaction is



However, the thermodynamic data suggest that the actual reducing agent is carbon monoxide [78]:



Barium sulfite, BaSO_3 , is an intermediate [79]. The CO forms in the reaction between carbon and CO_2 , the Boudouard equilibrium:



The barite should have a BaSO_4 content ≥ 95 wt %. Large amounts of impurities, especially silica and iron oxide, reduce the yield of water-soluble barium sulfide by forming the insoluble barium silicates and ferrates. The spar is ground to 0.1–2 mm and mixed with low-ash reducing carbon or coke, one part of carbon to 4–6 parts of barite.

Today the reduction is usually carried out in a continuous process centered around rotary kilns up to 50 m long. A burner at the outlet of the kiln fired with fuel oil, natural gas, or coal dust provides countercurrent heating. Reduction takes place at 900–1200 °C; average residence time is 90–120 min. The operating conditions must be carefully controlled to prevent secondary reactions with the gangue and to impede caking. The barium sulfide melt should be obtained in a fine-grained condition. The sulfide melt leaves the kiln continuously through a cooling drum. Generally further grinding is not necessary.

Various processes using a fluidized-bed kiln have been reported. Here, the pulverized spar, e.g., from flotation, is granulated together with carbon and reacted in a fluidized bed, a part of the carbon being used for heat generation and a part for reduction [79, 80]. Other processes use a reducing gas, e.g., carbon monoxide or methane,

instead of carbon. The gas serves three functions: it provides heat upon combustion, it supports the fluidization, and it is the reducing agent. The advantages are a reduction temperature below 1000 °C, a residence time less than 1 h, and a more favorable energy balance [81, 82]. However, large-scale plants of this kind have not been reported.

Crude barium sulfide (black ash) is *leached* countercurrently with 60–80 °C water to dissolve the barium sulfide. This leaching is carried out batchwise in batteries of Shank leaching vats or continuously in closed agitated vessels followed by several thickeners. The suspended matter is filtered off, and the lye, containing 13–18 % BaS, is immediately treated further to prevent oxidation or crystallization. At this point the barium sulfide solution is very pure.

The residue still contains 50 % barium, in the form of compounds insoluble in water, such as silicates and ferrates of barium and unreacted barite. The silicates and ferrates can be dissolved with hydrochloric acid to form barium chloride; however, this process is often uneconomical because of the cost of purifying the barium chloride solution. To avoid these problems it has been proposed that the leaching residue be re-suspended in water and, by adding hydrogen sulfide, the portion of barium compounds that are insoluble in water be converted into readily soluble barium hydrosulfide that can be led back into the sulfide lye [83].

Quality Specifications. Barium sulfide is available only as a technical-grade, granular, dark gray crude product called black ash. It contains 75–85 % water-soluble BaS, barium compounds soluble in hydrochloric acid (8–10 % as BaO), 2–4 % SiO_2 , 2–3 % Fe_2O_3 and Al_2O_3 , 2–4 % BaSO_4 , and 1–2 % carbon. The economic value depends directly on the content of water-soluble BaS, which is determined analytically by acidimetry and iodometry.

Packing and Shipping. Barium sulfide is packed in 25 kg paper bags with an inner polyethylene bag. Shipment is governed by IMDG Class 6.1, UN 1564, and RID/ADR Class 6.1, 60c.

Uses. Barium sulfide is mainly used for the production of other barium compounds, especial-

ly blanc fixe and lithopone. Some BaS is used for the production of hydrogen sulfide; in this case, barium chloride is the byproduct. Other uses (depilatories, purification of mineral acids) are far less important.

Barium Polysulfides. The polysulfides [50864-67-0] have the general composition BaS_x ($x = 2-5$). They include barium disulfide [12230-99-8], BaS_2 ; barium trisulfide [12231-01-5], BaS_3 ; barium tetrasulfide [12009-34-6], BaS_4 ; barium tetrasulfide monohydrate [12448-67-8], $\text{BaS}_4 \cdot \text{H}_2\text{O}$; barium tetrasulfide dihydrate [12231-03-7], $\text{BaS}_4 \cdot 2 \text{H}_2\text{O}$; and barium pentasulfide [12448-68-9], BaS_5 . Polysulfides form when barium sulfide solutions are oxidized by air, when sulfur is dissolved in barium sulfide solutions, when barium sulfide is fused with sulfur in a vacuum, etc.

The isolation of individual polysulfides from solution is difficult because of their tendency to decompose. Technical barium polysulfide can also be produced by grinding barium sulfide with sulfur ($\text{Ba}:\text{S} = 1:4-5$). It is marketed as a grayish-yellow powder. The formation of polysulfide does not take place until the powder is dissolved.

One process, however, produces a mixture of true barium polysulfides, BaS_{4-5} , by sudden evaporation of a solution in a spray dryer [84]. The resulting light yellow powder is stable and dissolves in water without leaving a residue.

As a 1-3% solution, barium polysulfide is a fungicidal and acaricidal agent used in fruit and grape growing.

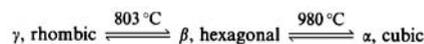
Shipment of barium polysulfides is governed by the IMDG Class 6.1, UN 1564, or RID/ADR Class 6.1, 60c.

2.4. Barium Carbonate

Barium carbonate is the most important manufactured barium compound after blanc fixe. It occurs in nature as witherite, which has little economic significance due to rareness, inevitable impurities, and almost fully depleted deposits.

Properties. Barium carbonate [513-77-9], BaCO_3 , M_r 197.35, mp 1360 °C accompanied by loss of CO_2 . Pure barium carbonate is a white

fine crystalline powder having several modifications:



The rhombic modification is isomorphous with the carbonates of calcium (aragonite), strontium (strontianite), and lead (cerussite).

Barium carbonate has a density of 4.29 g/cm^3 . Its solubility in water at 20 °C is only 2×10^{-3} wt %, although it is a little more soluble in water containing CO_2 . Its refractive index is ≈ 1.6 . Its heat capacity c_p at room temperature is 433 $\text{J kg}^{-1} \text{K}^{-1}$.

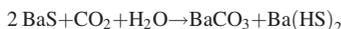
When barium carbonate is heated, it loses carbon dioxide and forms barium oxide. The dissociation is promoted by traces of water. Barium carbonate and its decomposition product barium oxide are partially soluble in each other at elevated temperatures, at 1000 °C ≈ 10 mol % oxide in the carbonate and ≈ 5 mol % of carbonate in the oxide—this partial solubility was not adequately appreciated in the older literature. Moreover, there is a eutectic at 1060 °C with 34 mol % barium oxide. The equilibrium CO_2 pressure above barium carbonate saturated with oxide increases rapidly above 1000 °C [85, 86]:

°C	900	1000	1100	1200	1250	1300	1360
kPa	0	0.21	1.6	10.1	21.6	46.4	101.3
Torr	0	1.6	12	76	162	348	760

Production. Barium carbonate is produced almost exclusively by precipitation from barium sulfide solutions. There are two processes:

1. precipitation with carbon dioxide
2. precipitation with soda

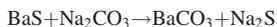
The first is based on the reactions



The carbon dioxide is usually available from combustion gases or native carbonic acid. The precipitation is carried out batchwise in gastight vessels, several of which may be arranged in series to absorb the carbon dioxide that breaks

through with the hydrogen sulfide in fresh lye; a utilizable hydrogen sulfide poor in carbon dioxide is produced in this way. Also there are continuous processes, e.g., using precipitation columns [87, 88].

The second process is based on the reaction



The barium sulfide lye containing 15–18 wt % BaS is run into \approx 30 wt % soda solution in agitator vessels.

The decision to favor one or the other of the two processes does not depend only on the availability and relative cost of carbon dioxide or soda. Above all else the value or sales prospects of the byproducts, H_2S or Na_2S , is decisive. The hydrogen sulfide must be worked up to sulfur, sulfuric acid, sodium hydrosulfide, or sodium sulfide. The dilute sodium sulfide solution produced in the soda process in most cases is upgraded to crystalline sodium sulfide hydrate (60 wt % Na_2S).

The main impurity in BaCO_3 , sulfur as sulfide, elemental sulfur, or sulfate, is the major problem. Patents offer a number of solutions: adding aluminum powder to the barium sulfide lye to reduce the polysulfide sulfur [89]; continuously maintaining a residual barium sulfide content in the solution of \approx 0.5 wt % during the precipitation with carbon dioxide to keep the sulfur dissolved [90]; or a careful step-by-step precipitation, perhaps first to BaCO_3 and $\text{Ba}(\text{HS})_2$ and then to BaCO_3 and H_2S [87, 88].

Quality Specifications. Purity, bulk density, and grain-size distribution depend on the particular use. Usually, low sulfur and heavy-metal content is demanded. The manufacturers of electroceramics require low strontium content. The numbers below refer to products of various origin, quality, and process and should only be regarded as reference values:

Barium carbonate	\geq 98.5 %
Sulfur	0.08 (0.02) %
Strontium	0.5–1.4 (0.3) %
Iron	$6\text{--}20 \times 10^{-4}$ %
Insoluble in $\text{HCl}_{(\text{soln})}$	0.1–0.6 %
Density	4.29 g/cm^3
Bulk density, tamped	0.4–1.8 (2.2) g/cm^3
Grain size, $< 5 \mu\text{m}$	80–95 %

An important standard for barium carbonate as a sulfate-binding agent is its reactivity. This is determined by conversion of barium carbonate with known quantities of sulfate, as gypsum water or sodium sulfate solution.

Packing and Shipping. Barium carbonate is stored in silos and shipped in multilayer paper bags, big bags, or silo wagons. Shipment is governed by the IMDG Class 6.1, UN 1564, or RID/ADR Class 6.1, 60c.

Uses. Barium carbonate is used to remove the detrimental sulfate ion from the input solutions of the chlor-alkali electrolysis, e.g., the mercury process, as well as from industrial waters of various kinds. In brick production, barium carbonate is a binder for the soluble sulfates in the raw mixture. The formation of insoluble barium sulfate prevents discoloration (efflorescence) during production. Moreover, barium carbonate reduces the tendency of baked bodies to effloresce on exposure to moisture. Barium carbonate is used to incorporate barium oxide into special fine glassware, apparatus glass, and many optical glasses. The barium oxide increases the workability of the glass melt, improves the mechanical and chemical resistance, and increases the density and refractive index of the glass.

Barium in television screens prevents the leakage of X rays. In the western world, the demand for cathode ray tube (CRT) televisions is declining since LCD (liquid crystal displays) and plasma screens are increasingly being used. As CRT televisions are, however, much cheaper, they are still favored in India and China, where most CRT production is still based.

Barium carbonate is also used in enamels and for the production of the electroceramic barium titanate [12047-27-7] and the magnetoceramic barium ferrites [12047-11-9]. These last two uses require high-purity BaCO_3 . Barium carbonate is also used in the synthesis of high-temperature superconductors.

2.5. Barium Chlorate

Barium chlorate monohydrate [10294-38-9], $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$, M_r 322.26, forms monoclinic short prismatic crystals of density $3.18 \text{ g}/\text{cm}^3$.

Its solubility in water is 21.2 wt % at 10 °C and 51.3 wt % at 100 °C. Near 120 °C barium chlorate begins to lose its water of crystallization, and above 250 °C oxygen is lost. The anhydrous salt melts at 415 °C; however, explosions can occur on fusion or if a mixture with sulfur or organic substances is heated even at 110 °C. Barium chlorate is a good oxidant.

Barium chlorate is produced on an industrial scale by mixing concentrated barium chloride solution into hot concentrated sodium chlorate solution. On cooling, barium chlorate monohydrate crystallizes. Although it crystallizes in a rather pure form, barium chlorate can be purified even further by recrystallization. This double conversion is more economical than electrolysis of a barium chloride solution, a process that is no longer used.

Barium chlorate is almost exclusively used in pyrotechnics, where it produces a green color. In addition, it has been used as an oxidizing agent, e. g., in textile printing. Shipment is governed by IMDG Class 5.1, UN 1445, or RID/ADR, Class 5.1, 29b.

2.6. Barium Chloride

Anhydrous barium chloride [10361-37-2], BaCl_2 , M_r 208.25, m_p 962 °C, ρ_{20} 3.91 g/cm³, crystallizes in two modifications: α - BaCl_2 (rhombic, mostly lamelliform) and β - BaCl_2 (cubic). The conversion temperature is 925 °C. Barium chloride is soluble in water:

°C	0	20	40	60	80	100
wt % BaCl_2	23.6	26.3	29.0	31.6	35.0	36.6

The enthalpy of fusion is 193 kJ/kg, and the entropy of fusion is 87.7 J kg⁻¹ K⁻¹. The heat capacity c_p is 361.8 J kg⁻¹ K⁻¹ near room temperature.

Barium chloride crystallizes from aqueous solutions as the dihydrate [10326-27-9], M_r 244.31, in monoclinic colorless plates, ρ 3.097 g/cm³. Water of crystallization is not lost much before 110 °C, this process being finished around 160 °C.

Production. Today the production of barium chloride on an industrial scale is carried out

by the reaction of 15–18 wt % barium sulfide solution with 31–32 wt % hydrochloric acid. In addition, the reaction of barium sulfide solution with chlorine is of commercial interest.

In both methods, reaction is continued until the solution becomes acidic to assure complete conversion of the barium sulfide and to remove from solution the hydrogen sulfide formed. The reaction with hydrochloric acid is often followed by oxidation with air or chlorine to convert any dissolved sulfur compounds into barium sulfate, which removes the sulfur from the solution. In both methods, the solution is neutralized afterwards with barium carbonate or sodium hydroxide to precipitate heavy metals.

The solubility of BaCl_2 in water does not depend strongly on temperature. If the barium chloride is to be crystallized, this is carried out by evaporative crystallization. In most cases, vacuum evaporation is used, the salt crystallizing as the dihydrate. Normally it is only dried but it can be dehydrated further if necessary. The mother lye, which still contains barium chloride, can be processed to produce insoluble blanc fixe (BaSO_4) or barium carbonate. The byproduct hydrogen sulfide from the hydrochloric acid process can be converted into sodium sulfide or sodium bisulfide or oxidized to produce sulfuric acid.

In the chlorine process, the byproduct is sulfur, usually containing barium carbonate and heavy metals.

Byproduct barium chloride is obtained in the production of lithopone grades containing more than 30 wt % zinc sulfide, for in these cases barium sulfide is reacted with zinc sulfate and zinc chloride. Another source of barium chloride is the black ash leaching residues. These are reacted with hydrochloric acid by some manufacturers. However, the resulting barium chloride solutions contain such a concentration of impurities that they must be purified extensively before further use.

The literature reports various procedures to convert barite directly into barium chloride. These procedures, e.g., the reaction of barite with carbon and calcium chloride or the chloridizing reduction of barite, no longer have significance in Western Europe or America, for they are now uneconomical. Direct conversion may still be of interest in Eastern Europe, where numerous scientific papers and patents on direct conversion

have been issued, e.g., [91]. The industrial production of barium chloride from barium sulfate, carbon, and calcium chloride is reported only from the People's Republic of China.

Quality Specifications, Packing, Shipping. Both the dihydrate and anhydrous barium chloride are marketed as technical grades of 99–99.5%, the dihydrate also being available as a high-purity grade ($\approx 100\%$). They are packed in 50 kg multilayer paper bags with polyethylene covers or liners to protect against moisture. Shipment is governed by IMDG Class 6.1, UN 1564 (harmful, keep separate from foodstuffs), or RID/ADR Class 6.1, 60c.

Uses. Along with other chlorides, barium chloride is used as a component of melt quenching baths for steel. It is used as a starting material for the production of sulfide-free blanc fixe grades and, instead of barium carbonate, to remove sulfate from solutions. Finally, it has a limited importance as a stabilizer for plastics.

2.7. Barium Ferrite

Barium hexaferrite [12047-11-9], $\text{BaFe}_{12}\text{O}_{19}$, M_r 1111.49, forms hexagonal needle-shaped ferromagnetic crystals. It is usually manufactured in a two-stage solid-state reaction, first stage at 650–750 °C, second stage > 850 °C. An intermediate is barium monoferrite [12009-00-6], BaFe_2O_4 (\rightarrow Magnetic Materials).

2.8. Barium Oxide

Barium oxide [1304-28-5], caustic baryta (an older term), BaO , M_r 153.33, $m_p \approx 1920$ °C, sublimes ≈ 2000 °C. Pure commercial barium oxide is a white fine crystalline powder, whereas technical grades are often gray due to carbon impurities. Barium oxide forms face-centered cubic crystals. The densities reported in the literature vary considerably, perhaps depending on preparation. The most likely value is ≈ 5.7 g/cm³.

Usually barium oxide is very reactive. However, its reactivity depends on the preparative conditions, the reaction temperature, and the coreactant. In the absence of water, BaO often

reacts very slowly with carbon dioxide. In the presence of small amounts of water, however, it is converted by carbon dioxide into barium carbonate in a very exothermic reaction. The conversion of barium oxide by water into barium hydroxide is also very exothermic. Self-ignition may occur on contact with wet organic substances. Barium oxide is soluble in methanol: 20 wt% dissolves at 15 °C, and therefore barium oxide can be purified by recrystallization before it is used as a starting material for organic barium compounds or for incorporation, as a methylenate, into organic systems.

Production. Barium oxide is mainly produced by decomposition of barium carbonate in the presence of carbonaceous material at high temperature. The use of carbon significantly lowers the temperature at which the barium carbonate decomposes, which to a large extent avoids unwanted corrosion of the reactor when barium carbonate is decomposed by heat alone at 1400 °C. Also important is the decomposition of barium carbonate mixed with channel black (6.2 wt% C) in retorts of silicon carbide – corundum externally heated to ≈ 1250 °C.

The modern procedures tend to use continuous fluidized beds. Barium carbonate – soot pellets are used [92, 93], or the carbon is added to the fluidized bed as methane [94]. The advantages are, among others, that the low reaction temperatures give less-sintered products, i.e., more reactive BaO .

There are also procedures using electrical arcs in a core zone [95]. In such processes a steep temperature drop is maintained between the hot core zone and the reactor shell, to provide a protective layer for the shell material. Addition of carbon is not absolutely necessary.

The crude barium oxide can be reacted [93, 94] in a second stage with carbon for more complete conversion.

Quality Specifications. Barium oxide is marketed in grades of a purity of 97–99 wt%. The main impurities are 1–3 wt% barium carbonate, ≤ 1 wt% barium peroxide, and a few tenths of a percent of nonconverted carbon.

Storage and Shipping. Barium oxide is shipped mainly in iron drums or, for smaller quantities, in tin cans. Shipment is governed by

the regulations on the transport of harmful goods of the IMDG Class 6.1, UN 1884, or RID/ADR Class 6.1, 60c.

Uses. Barium oxide, like barium hydroxide, is mainly used for the preparation of additives for oils and greases; however, this is losing significance. In addition, barium oxide is used as a starting material for organic barium salts used in plastics. Barium oxide is frequently used in the production of luminescent materials.

2.9. Barium Peroxide

Barium peroxide [1304-29-6], BaO_2 , M_r 169.33, → Peroxo Compounds, Inorganic, Section 2.1.2..

2.10. Barium Hydroxide

The anhydrous hydroxide has only a secondary industrial importance; the monohydrate and octahydrate are used in industry on a far larger scale.

Properties. Barium hydroxide octahydrate [12230-71-6], hydrate of baryta, caustic baryta, $\text{Ba}(\text{OH})_2 \cdot 8 \text{H}_2\text{O}$, M_r 315.47, forms monoclinic pseudotetragonal crystals, often plates when rapidly crystallized. It dissolves at 78 °C in its own water of crystallization, releasing the water when heated above 108 °C to yield the monohydrate. The enthalpy of melting is high at a value of 280 J/g. The density is $\approx 2.18 \text{ g/cm}^3$. The specific heat capacity c_p of the solid is 1250 J $\text{kg}^{-1} \text{K}^{-1}$, of the melt 1675 J $\text{kg}^{-1} \text{K}^{-1}$ at 80 °C.

The solubility in water depends dramatically on the temperature:

°C	0	20	40	60	78
wt % $\text{Ba}(\text{OH})_2 \cdot 8 \text{H}_2\text{O}$	3.0	6.9	14.1	32.6	100.0
g $\text{BaO}/100 \text{ g H}_2\text{O}$	1.5	3.48	7.35	18.8	94.7

The solutions are strongly alkaline and tend to supersaturate.

Like all soluble hydroxides, barium hydroxide, especially in aqueous solution, reacts readily with acidic gases. The most important example in

practice is carbon dioxide, to form barium carbonate.

Barium hydroxide monohydrate [22326-55-2], $\text{Ba}(\text{OH})_2 \cdot \text{H}_2\text{O}$, M_r 189.37, crystallizes as often radially intergrown needles. Its density ρ_{20} is $\approx 3.74 \text{ g/cm}^3$. The monohydrate does not react with dry carbon dioxide.

Anhydrous barium hydroxide [17194-00-2], $\text{Ba}(\text{OH})_2$, M_r 171.35, $mp \approx 407 \text{ °C}$. The course of the dehydration, i.e., the temperatures and times, from monohydrate to anhydrous $\text{Ba}(\text{OH})_2$ depends on the reactivity of the monohydrate. Molten anhydrous hydroxide is so corrosive, attacking steel and most ceramics, that the conversion of barium hydroxide into barium oxide, which takes place at 800 to 850 °C, is not carried out on an industrial scale.

Production. Barium hydroxide octahydrate can be produced by hydration of barium oxide. The barium oxide is suspended in recycled mother liquor and heated for several hours to destroy peroxides. The insolubles, e.g., BaCO_3 , are separated, and the hydroxide is precipitated by crystallization at low temperatures in stainless steel vessels. The crystals are removed from the mother lye by centrifugation.

Another industrial method is based on the oxidation of a barium sulfide solution [96–98]. Air is passed into the stirred solution containing barium hydroxide and barium hydrosulfide, the hydrolysis products of barium sulfide, until the hydrosulfide is oxidized to form polysulfide. Then the barium hydroxide octahydrate is crystallized at low temperatures and separated with a centrifuge. The polysulfidic mother liquor is partly recycled; the rest is usually processed into other barium compounds. The advantage of this procedure over the direct reaction of BaS solutions with NaOH is the lower strontium content of the barium hydroxide product.

The monohydrate is generally produced on a commercial scale by dehydration of the octahydrate in heated vacuum driers. A monohydrate of especially high reactivity is obtained with drum driers [99]. This highly reactive monohydrate is particularly suitable for the production of oil additives, PVC stabilizers, and catalysts.

Storage, Packing, Shipping. Both the monohydrate and the octahydrate are packed and stored in 25 or 50 kg polyethylene-lined multi-

layer paper bags or in big bags. Shipping is governed by IMDG Class 6.1, UN 1564, or RID/ADR Class 6.1, 60c.

Uses. Barium hydroxide, especially the monohydrate, is used to produce organic barium compounds such as additives for oil and stabilizers for plastics. In addition, barium hydroxide is used for dehydration and deacidification, especially for removing sulfuric acid from fats, oils, waxes, and glycerol. In some applications, e.g., removal of sulfate from water and as starting material for other barium compounds, barium hydroxide to some extent replaces barium carbonate. The earlier use of the hydroxide in some countries for extracting the residual sucrose from molasses is no longer of much significance. The patent literature describes a procedure in which barium hydroxide is reacted with hydrogen peroxide to produce barium peroxide monohydrate [100].

2.11. Barium Nitrate

Barium nitrate [10022-31-8], $\text{Ba}(\text{NO}_3)_2$, M_r 261.34, mp 593 °C, colorless cubic crystals, often octahedra, Q_{20} 3.24 g/cm³. The solubility of barium nitrate in water increases with temperature:

°C	0	10	20	50	100
wt % $\text{Ba}(\text{NO}_3)_2$	4.8	6.5	8.4	14.6	25.4

On heating, barium nitrate decomposes into barium oxide, barium peroxide, nitric oxide, nitrogen, and oxygen. The gaseous products formed and their proportions depend largely on the temperature and rate of heating [101]. The presence of sulfur or organic substances may cause an explosion.

For the *production* of barium nitrate, various procedures are possible, starting from BaCO_3 , $\text{Ba}(\text{OH})_2 \cdot 8 \text{H}_2\text{O}$, BaS , or BaCl_2 . However, for industrial production there are two main procedures. In the first, barium carbonate is suspended in recycled mother lye and reacted with nitric acid. If necessary, heavy metals are precipitated, and the solution is filtered hot. The nitrate is then crystallized, if necessary with vacuum evapora-

tion. The second procedure consists of reacting a barium sulfide solution, directly or after the removal of barium hydroxide, with nitric acid. After carefully removing any sulfur formed and the heavy metals, the barium nitrate is crystallized at low temperatures.

The preparation of $\text{Ba}(\text{NO}_3)_2$ by double conversion of barium chloride and sodium nitrate or calcium nitrate is described in the Eastern European patent literature.

Barium nitrate is packed and stored in 25 kg polyethylene-lined multilayer paper bags. Shipping is governed by IMDG Class 5.1, UN 1446, or RID/ADR Class 5.1, 29b.

One of the main uses, as a component in pyrotechnics to produce a green color, requires very pure barium nitrate, 99.5–99.8%. The content of other flame colorants – sodium, strontium, calcium – must be extremely low. Barium nitrate is used as a plaining agent in the manufacture of special glasses and optical glasses in place of the combination alkali-metal nitrate – arsenic. In addition it is used to incorporate barium oxide into catalysts, in luminescent cathode-ray screens, and as a component of metallurgical hardening agents.

2.12. Barium Titanate

Barium titanate [12047-27-7], BaTiO_3 , M_r 233.24, mp 1625 °C, Q_{20} 6.02 g/cm³, has phase transitions and both ferroelectric and piezoelectric properties (→ Ferroelectrics; → Insulation, Electric).

2.13. Barium Salts of Organic Acids

Barium acetate is used as a mordant in the printing industry and as a catalyst in organic chemistry.

Barium stearate is used as a slip agent in plastics and metal working, as a stabilizer against heat and light in PVC, and also in the production of grease.

The compound known as barium octoate is normally the barium salt of 2-ethylhexanoic acid. It is used as a siccative (drying agent) for the curing of alkyd paints. Siccatives catalyze the reaction between double bonds of the resin and atmospheric oxygen.

Certain dyes and pigments, also known as lakes, contain barium either as the salt of a carboxylic acid group or of a sulfonic acid group within the molecule. Well-known examples are the β -naphthol azo pigments [102].

3. Barium in the Environment

The terrestrial abundance of barium is approximately 250 g/t [10]. The estimated average barium concentration in the soil is 500 g/t [103]. Measured concentrations range between 100 and 3000 g/t [104].

Barium occurs in seawater in a concentration of 6 $\mu\text{g/L}$ [105]. This level is due to reaction between barium and sulfate ions also present in the oceans. The concentration of barium is higher in deep ocean waters than in surface ocean waters [11]. The precipitated barium sulfate forms a permanent part of the sediment on the ocean floor [106]. In fresh water the barium content depends upon the occurrence of barium and the concentration of anions which form barium salts of low solubility such as sulfate and carbonate ions. Values between 7 and 15 000 $\mu\text{g/L}$ (average: 50 $\mu\text{g/L}$) have been reported [107].

Studies of drinking water gave a wide range of values between only traces and 10 000 $\mu\text{g/L}$ in the USA [119], 5–600 $\mu\text{g/L}$ in Canada [120], and 1–20 $\mu\text{g/L}$ in municipal drinking waters in Sweden [107].

Barium levels in the air are not well documented. An estimate of a mean value for the USA is 0.05 $\mu\text{g/L}$ [121]. There is no correlation between the degree of industrialization and the barium concentration in the air. Higher levels are found in areas with high natural dust levels. Anthropogenic emissions are primarily industrial. Reports about the release of barium by way of exhaust gases, mainly from diesel engines [122, 123], are no longer valid since in the last few years the primary cause, namely, the sulfur content of diesel fuels, has been reduced due to legislation. Therefore, there is no longer a need to use barium compounds as sulfur-scavenging fuel additives. Other atmospheric emissions result from the handling of barium compounds or materials containing barium compounds, such as welding wires [124].

4. Dietary Intake of Barium

Figures for the mean dietary intake of barium in the USA ranged from 300 to 1700 $\mu\text{g/d}$ [125] and 650 to 1770 $\mu\text{g/d}$ in two other studies [126]. These results match well with barium intakes in other parts of the world [127] with reported levels between 80 and 1330 $\mu\text{g/d}$. Apart from drinking water, milk, potatoes, and flour have been suggested to be the main sources for barium in the diet [128], even though absolute barium concentrations are higher in, for example, eggs and certain types of cheese. The normal dietary intake of barium within these limits is apparently harmless to humans. Acute symptoms will, however occur in case of an overdose of bioavailable barium (see Chap. 5). There is no evidence that barium is carcinogenic [121].

Typical levels of barium in human tissues and blood [11]: 3–70 ppm in the bone; 0.04–1.2 ppm in the liver; 0.09 ppm in the muscle, and 0.06 mg/dm^3 in the blood. The total mass average for a 70-kg human is 22 mg.

5. Toxicology

Water-soluble barium compounds are toxic, as is shown in Table 4. Most barium poisonings are caused by mistaking soluble barium compounds, such as barium carbonate, for the insoluble – and therefore nontoxic – barium sulfate, which is used as a contrast agent in X-ray diagnosis.

The symptoms of poisoning are convulsions of both striated and smooth muscles, including the heart, followed by paralysis of the peripheral nerve system. These effects on the nerve system

Table 4. Acute lethal doses of soluble barium compounds

Compound	Toxicity	Ref.
Barium carbonate [513-77-9]	TDLo 29 mg/kg (human, oral)	[108]
Barium nitrate [10022-31-8]	LD ₅₀ 8.5 mg/kg (mouse, i.v.) LD ₅₀ 355 mg/kg (rat, oral)	[109] [110]
Barium chloride [10361-37-2]	LDLo 11.4 mg/kg (human, oral)	[111]
Barium oxide [1304-28-5]	LD ₅₀ 50 mg/kg (mouse, subcutaneous)	[112]
Barium fluoride [7787-32-8]	LD ₅₀ 250 mg/kg (rat, oral)	[113]

are accompanied by severe inflammation of the gastrointestinal tract.

Barium carbonate is often used in the ceramics industry. Detailed examination of workers exposed to BaCO₃ dust for 7–27 years did not reveal any specific chronic poisoning [114]. Damage to the lungs has been reported to have been caused by contaminants in the barium compounds, such as quartz [115] or zinc sulfide [116]. However, BaSO₄ may cause a benign pneumoconiosis (barytosis) because, unlike BaCO₃, BaSO₄ is not absorbed by the organism [117, 118]. The legally binding “Permissible Exposure Limit” (PEL) for BaSO₄ dust in the USA is 15 mg/m³, whereas the voluntary “Threshold Limit Value” (TLV) was set to 10 mg/m³. The German MAK value for BaSO₄ dust is 3 mg/m³.

For soluble barium compounds, an exposure limit of 0.5 mg/m³ (as Ba) has been established by both TLV (1989) and MAK (1996) commissions. According to the MAK, short-term exposure limits may be as high as 1 mg/m³ (average over 30 min, four times within 8 h).

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