BARIUM

1. Introduction

Barium [7440-39-3], Ba belongs to Group 2. (IIA) of the Periodic Table. Calcium, strontium, and barium belong to the alkaline earth metals and form a closely allied series in which the chemical and physical properties of the elements and their compounds vary systematically with increasing size, ionic and electropositive nature, and specific density. The properties are greatest for barium.

In 1774, Scheele determined that barium oxide was a distinct oxide or "earth," and named it terra ponderosa because of its high density (1). Later, this name was changed to barote from the Greek word meaning heavy. Later still, the name of the oxide was modified to baryta to conform to the nomenclature recommended by Lavoisier, and from this the name barium was derived.

After many unsuccessful attempts, Davy produced barium as a mercury amalgam in 1808 by electrolyzing barium chloride in the presence of a mercury cathode. Attempts were made to isolate the pure metal by distilling the mercury, but it is doubtful that metal of high purity was ever obtained. Early in the twentieth century, high purity barium was prepared by heating barium amalgam in a stream of hydrogen, thereby converting the barium to a hydride and simultaneously volatilizing the last traces of mercury. The pure metal was then obtained by thermal decomposition of the hydride followed by condensation of the volatile barium vapor (1).

Barium is prepared commercially by the thermal reduction of barium oxide with aluminum. Barium metal is highly reactive, a property that accounts for its principal uses as a getter for removing residual gases from vacuum systems and as a deoxidizer for steel and other metals.

In metallic form, barium reacts readily with water to release hydrogen:

$$Ba + 2\,H_2O \longrightarrow Ba(OH)_2 + H_2$$

In aqueous solution it is present as an ion with +2 charge.

2. Ocurrence

In its natural form, barium never occurs as the metal because of reactivity, but is almost always found as the ore barite [13462-86-71], $BaSO_4$, which is also known as heavy spar. A smaller deposit is found as barium carbonate, $BaCO_3$ (witherite) [14941-39-0] barium carbonate can easily be decomposed by heating (calcination) to BaO. Barium oxide is used commercially for the production of barium metal.

3. Physical Properties

Pure barium is a silvery white metal, although contamination with nitrogen lead to a yellowish color. The metal is relatively soft and ductile and may be worked readily. It is fairly volatile (though less than magnesium) and this property is used to advantage in commercial production. Barium has a body-centered entered cubic (bcc) crystal structure at atmospheric pressure, but undergoes structural phase transitions at high pressure (2,3). Barium also exhibits hig ressure induced superconductivity at low temperatures (4,5) and is an essential component of several high temperature superconductors eg, $YBa_2Cu_3O_7$ (6).

It is not easy to obtain samples of ultrahigh purity, and therefore accurate 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. Physical properties of barium are listed in Table 1.

4. Chemical Properties

Barium has a valence electron configuration of $6s_2$ and characteristically forms divalent compounds. It is an extremely reactive metal and its compounds possess large free energies of formation. At room temperature, it combines readily and exothermically with oxygen and the halogens. It reacts vigorously with water, liberating hydrogen and forming barium hydroxide [17194-00-2], $Ba(OH)_2$. At elevated temperatures, barium combines with hydrogen to form barium hydride [13477-09-3], BaH_2, and with nitrogen to form barium nitride [12047-79-9], Ba_3N_2. With nitrogen and carbon, barium forms a cyanide that is thermally stable.

Finely divided barium is susceptible to rapid, violent combination with atmospheric oxygen. Therefore, in powdered form it must be considered pyrophoric and very dangerous to handle in the presence of air or other oxidizing gases. Barium powder must be stored under dry argon or helium to avoid the possibility of violent explosions. Large pieces of barium, however, oxidize relatively slowly and present no explosion hazard if kept dry.

Most barium compounds are not as thermodynamically stable as the corresponding compounds of magnesium and calcium, and therefore, can be reduced

Table 1. **Physical Properties of Barium**[a]

Physical properties						Value
atomic number						56
relative atomic mass A_r						137.34
mass number (natural abundance, %) of stable isotopes:						130 (0.101), 132 (0.097), 134 (2.42), 135 (6.59), 136 (7.81), 137 (11.3), 138 (71.7)
density at 20°C, g/cm^3						3.74
melting point °C						726.2
boiling point, at 101.3 kPa, °C[b]						1637
hardness (mohs scale)						1.25
crystal structures						bcc
lattice constant α_0 at 20°C nm						0.5025
coefficient of thermal expansion, α_1, (mean, 0–100°C)						$1.8\times10^{-5}\,\mathrm{K}^{-1}$
modulus of elasticity N/m^2						1.265×10^{10}
heat of fusion, ΔH_m, kJ/mol[c]						7.98
heat of vaporization, ΔH_v, kJ/molc						140.3 kJ/mol
specific heat capacity c at 20°C J/hg·K						192 J
at 900°C, J/hg·K						230 J kg
Vapor pressure at						
temperature, °C	630	730	1050	1300	1520	1637
pressure, kPa	0.00133	0.0133	0.133	13.3	53.3	101.3
Electrical resistivity, Ω cm						40×10^{-6}
commercial purity						
extra high purity						30×10^{-6}
liquid barium at mp						314×10^{-6}
Thermal coefficient of electrical resistivity $d\rho/dT$ (mean, 0–100°C)						$6.5\times10^{-3}\mathrm{K}^{-1}$

[a] Ref. 7

[b] To convert kPa to mm Hg, multiply by 7.5.

[c] To convert J to cal, divide by 4.18.

by these metals. However, rather than producing pure barium, barium alloys are formed. Barium combines with most metals, forming a wide range of alloys and intermetallic compounds. Among the phase systems that have been b tter characterized are those with Ag, Al, Bi Hg, Pb, Sn, Zn, and the other Group 2 (II A) metals (8).

Barium reduces the oxides, halides, and sulfides of most of the less reactive metals, thereby producing the corresponding metal. However, calcium metal can, in most cases, be used for similar purposes and is usually preferred over barium because of lower cost per equivalent weight and nontoxicity (see ACTINIDES AND TRANSACTINIDES).

5. Manufacture and Processing

Barium metal is produced commercially by the reduction of barium oxide with a less reactive, nonvolatile element, usually aluminum (9–15):

$$4\mathrm{BaO} + 2\,\mathrm{Al} \longrightarrow 3\,\mathrm{Ba} + \mathrm{BaAl_2O_4}$$

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 $\approx 1100^\circ C$ in the segment 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 on the cooler part of the apparatus (16). It is collected and cast into chill molds under argon.

Production of ultrapure barium metal has been investigated on a laboratory scale. Redistillation (17,18), zone recrystallization (19,20), and combinations of these techniques (21) have been studied. Impurity levels of <100 ppm have been attained.

Barium production requires large amounts of energy for two reasons: the high temperatures required in the process itself and the energy-intensive raw materials employed, the calcined BaO and the electrolytically produced aluminum.

Because of its high reactivity, production of barium by such processes as electrolysis of barium compounds solution or high temperature carbon reduction is impossible. Electrolysis of an aqueous barium solution yields $Ba(OH)_2$, whereas carbon reduction of an ore such as BaO produces barium carbide [50813-65-5], BaC_2, which is analogous to calcium carbide (see CARBI DES). Attempts to produce barium by electrolysis of molten barium salts, usually $BaCl_2$, met with only limited success (22), perhaps because of the solubility of Barium in $BaCl_2$ (23).

6. Shipment, Storage, and Handling

6.1. Shipment. The barium crowns are usually broken into smaller pieces and can be sold in this form or cast or extruded into bars or wire. Usually, the metal is packaged filled plastic bags inside argon-filled steel containers.

Barium is commercially available in bars up to 20 kg or in rods 22 mm in diameter and 40 mm in length (24). 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 paraffin oil. Smaller amounts (1–10 kg) are packaged in tin cans, and even smaller samples are packaged in hermetically sealed glass bottles (25,26).

Barium is classed as a flammable solid and cannot be mailed. If it comes into contact with water, there is always the danger of explosion because of the liberated hydrogen. Therefore barium should always be stored in a dry, well-ventilated place and 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 (24):

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

6.2. Storage. Store barium metal in a sealed container away from water, acids, or organic compounds. Protect containers against physical damage. Avoid damaging container.

6.3. Handling.

Provide adequate exhaust ventilation to meet exposure limit requirements. An exhaust filter system may be required to avoid environmental contamination. Wear a positive pressure air-supplied respirator in situations where there may be a potential for airborne exposure. Wear impervious clothing including gloves to prevent contact with skin, also used goggles and on face shold.

7. Economic Aspects

Chemetall GmbH, Germany, is the leading producer of barium metal. Chemetall GmbH covers the global demand of berium metal and $BaAl_4$. Only little is known about its production in Russia and China.

Production or consumption figures are not available.

Price levels were not published in 1999. Price average value for barite are in 2001 was ~\$25/t, mine (27).

8. Grades, Specifications, and Quality Control

Barium metal is marketed in purities from 95% for technical applications to 99.5% for high purity applications.

Assays and purities of commercial products are derived by subtracting the sum of analyzed impurity levels from unity. Alkali metal impurities are analyzed by emmission spectroscopy, whereas alkalin earth metals are determined by atomic absorption. Other metals and anions can be determined by photometric methods. Chloride is established argentometrically.

9. Analytical Methods

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 acetic acid. Barium is determined gravimetrically by precipitation of the small quantities are determined spectrometrically (29).

The metallic impurities in commercial barium (see Table 2) are determined by atomic absorption and flame emission spectroscopy. Trace impurities are best determined by inductively coupled emission spectroscopy (ICP) (30). 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 $^{16}O(n,p) \rightarrow {}^{16}N$ is the recommended method for determination of oxygen in alkaline earth metals (31).

10. Environmental Concerns

The terrestrial abundance of barium is ~250 g/t (32). The estimated average barium concentration in the soil is 500 g/t (33). Measured concentrations range betweeen 100 and 3000 g/t (34).

Table 2. **Chemical Analysis of Commerical Barium**[a]

Element		%
barium	(incl. Sr)	99.2 ± 0.30
strontium	max.	0.8
calcium	max.	0.25
aluminum	max.	0.06
carbon	max.	0.06
magnesium	max.	0.02
nitrogen	max.	0.02
iron	max.	0.02
chlorine	max.	0.01
lithium, sodium, potassium	max.	0.01

[a] Ref. 24.

Barium occurs in seawater in a concentration of 6 μg/L (35). This level is due to reaction between barium and sulfate ions also present in the ocean. The precipitated barium sulfate forms a permanent part of the sediment on the ocean floor (36). ln fresh water, the barium content depends on the occurence of barium and the concentration of anions that form barium salts of low solubility such as sulfate and carbonate ions. Values between 7 and 15,000 μg/L (average: 50 μg/L) have been reported (37).

Studies of drinking water give a wide range of values between only traces and 10,000 μg/L in the United States (38–44) in Canada (45) and 1–20 μg/L in municipal drinking water in Sweden (37).

Barium levels in the air are not well documented. An estimate of a mean value for the United States 0.05 μg/L (46). There is no correlation between the degree of industrilization and the barium concentration in the air. Higher levels are found in areas with high natural dust levels. Anthropogenic emissions are primarily industrial. Other atmospheric emissions result from the handling of barium Co or materials containing barium compounds, such as welding wires (47).

11. Recycling and Disposal

Consult with environmental regulatory agencies for guidance on acceptable disposal practices.

12. Health and Safety Factors

Barium metal reacts with water and acids to form hydrogen gas, barium oxide, and barium hydroxide; the reaction is exothermic. If barium metal contacts moisture in the eyes, on the skin, or in the respiratory tract, severe corrosive irritation may result. Inhalation of dust or fume may cause severe respiratory irritation, cough, difficulty in breathing, and chemical pnemonitis. Contact with skin causes irritation and possible corrosive damage.

The substance is severely irritating to eyes and may injure eye tissue if not promptly removed.

> Ingestion may cause acute irritation or burns to the mouth, throat, and stomach; barium may cause vomiting. Preexisting chronic respiratory, skin, or eye diseases may be aggravated.
>
> The symptoms of inhalation include severe irritation of respiratory tract. Skin and eye contact symptoms are severe irritation.
>
> There are no known adverse health effects resulting from long-term exposure to barium metal.

Barium metal poisoning is virtually unknown in industry, although the potential exists when the soluble barium compound forms are used. When ingested or given orally, the soluble, ionized barium compounds exert a profound effect on all muscles and especially smooth muscles, markedly increasing their contractility. The heart rate is slowed and may stop in systole. Other effects are increased intertinal peristalsis, vascular constriction, bladder contraction, and increased voluntary muscle tension.

For soluble barium compounds an exposure limit of 0.5 mg/m^3 (as Ba) has been established by both TLV (1989) and MAK (1996) commissions.

12.1. First Aid

Eye contact. Flush eyes with a steady stream of water for at least 15 min. Lift upper and lower eye lids frequently. Get prompt medical attention.

Skin contact. Immediately remove and isolate contaminated clothing. Carefully brush off material from skin and wash affected area thoroughly with water. Call a physician if irritation develops. lnhalation. Remove to fresh air. If symptoms develop, seek immediate medical attention. If not breathing, give artificial respiration.

Ingestion. Call a poison control center, emergency room, or physician if barium is ingested. Unless advised otherwise, induce vomiting by giving either syrup of ipecac followed by two glasses of water. If a soluble barium compound has been swallowed, get medical attention. If the person is drowsy or unconscious, DO NOT GIVE ANYTHING BY MOUTH or leave alone. Never give anything to drink to a person who is convulsing or has no gag reflex. Loosen tight fitting clothing, clear the airway, and keep the person warm.

Note to physician: Treatment should be directed at preventing absorption, administering to the symptoms as they occur, and providing supportive therapy.

12.2. Fire Fighting and Explosion Hazards. Do not use water, foam, or halogenated hydrocarbons such as Halon or carbon tetrachloride to extinguish fire. Use only dry chemical/dolomite (powdered limestone), or an appropriate metal-fire-extinguishing dry powder, such as Met-L-X or Totalit M. For large fires, withdraw from the area and let the fire burn.

Firefighters should wear self-contained breathing apparatus with full face piece operated in the pressure-demand or positive-pressure mode. Firefighters should move containers from the fire area if this can be done without risk. Do not use water or foam. Use dry powder only.

Water reacts dangerously with barium metal and is not recommended as an extinguishing agent for fires. If water must be used, prevent it from coming into direct contact with barium metal. If contact is unavoidable, apply the water in flooding amounts to safely absorb the heat that will be generated.

Barium metal is extremely dangerous when wet. Barium metal forms barium hydroxide and hydrogen gas resulting in an explosion hazard when wet.

Barium metal forms BaO when it burns. It reacts with wet extinguishing agents such as water, halogens, and possibly carbon dioxide.

12.3. Accidental Release Measures.

Do not touch spilled barium metal. Wear protective apparel. Do not smoke or place flame or ignition sources near spill area. Do not allow water to touch spilled barium metal or to get inside containers. Use a cover to prevent water or rain from dissolving spilled barium metal or to prevent its spreading. Isolate hazard area and keep nonessential personnel away from spill or leak site. Shovel small dry spills into a dry container and cover it tightly. Move containers away from spill to a safe area. Take up small spills with sand or an absorbent and contain as described above. Dike the flow of large barium metal and water spills with soil, sandbags, or concrete. Keep the waste form entering drains and open sewers. Wear full protective gear.

13. Uses

The major use of barium is the production of barium–aluminum alloy—evaporation getters (gas absorbers) in CRTs (cathode ray tubes) for television sets and computer monitors to generate and to maintain high vacuum by reaction with detrimental gases. Barium is used as getter material in X-ray and emitter tubes and in sodium vapor lamps.

Because of its low vapor pressure and its reactivity toward gases, such as oxygen, nitrogen, hydrogen, carbon dioxide, and water vapor barium is an ideal getter material. The market demand of barium depends strongly on the demand for CRTs. The demand for CRTs has been increasing in the past few years. This is a result of increased demand for personal computers requiring color monitors.

Barium is also used to improve performance of lead alloy grids of acid batteries.

The deoxidizing and reducing properties of barium find numerous minor applications in the metal refining and alloying industry.

Many other uses of barium have been described in the literature, but they are of minor importance. Barium increases the creep resistance in lead–tin soldering alloys therefore it has been used in bearing alloys. Instead of strontium or sodium, barium has been used as a modifying agent for "silumin" where barium refines the structure of the eutectic aluminum–silicon alloy.

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Claudio Boffito
Saes Getters SpA