

LITHIUM AND LITHIUM COMPOUNDS

1. Introduction

Lithium [7439-93-2], Li, an element with unique physical and chemical properties, is useful in a wide range of applications.

Lithium was first identified in 1817 by Johan August Arfvedson working in the laboratory of Jöns Jakob Berzelius (1). The new element was named *lithos* from the Greek meaning stone. Minute amounts of metallic lithium were first prepared in 1818. Lithium was prepared in larger quantities simultaneously in 1855 by Robert Bunsen (Germany) and Augustus Matthieson (England).

Many of the properties of lithium are similar to those of magnesium and other of the alkaline-earth metals (see MAGNESIUM AND MAGNESIUM ALLOYS). This is in accord with the diagonal relationship principle of the Periodic Table. Resemblance to magnesium includes the high solubility of the halides (except the fluoride) in both water and polar organic solvents and the high solubility of the alkyls in hydrocarbons; the low aqueous solubility of the carbonate, phosphate, fluoride, and oxalate; the thermal instability of the carbonate and nitrate; the formation of the carbide and nitride by direct combination; and the reaction with oxygen to form the normal oxide.

The first commercial use of lithium occurred toward the end of World War I when small amounts were used in an aluminum–zinc alloy, Scleron. After that war lithium was used as a hardener in a lead alloy-bearing material, Bahnmetall. Between World Wars I and II there was little production of lithium materials. Most lithium trade was as ores sold as additives to frit and glass (qv) formulators. In 1942 lithium chemicals were needed for wartime efforts and commercial production of lithium salts, the metal, and metal derivatives increased. Lithium hydride [7580-67-8], LiH, was used in military sea rescue equipment to provide a source of hydrogen upon reaction with water. The hydrogen inflated rescue balloons to carry the radio antenna needed for the SOS signal broadcast. During this period, all-purpose temperature-resistant greases using lithium stearate [4485-12-5] were produced for military application.

Whereas new applications of lithium compounds were developed, commercial growth was slow. In 1953 worldwide sales of lithium products, expressed as lithium carbonate, were only ca 1000 metric tons (2). In 1954 the U.S. lithium industry underwent a sudden, very large expansion when the U.S. Atomic Energy Commission required large amounts of lithium hydroxide [1310-65-2] for its nuclear weapons program. Three domestic producers built 4500-t/yr plants to meet contract commitments with the U.S. government. When these government contracts ended in 1960, capacity exceeded demand and several operations were discontinued.

There has been significant growth in lithium and lithium compounds usage since 1960. Many commercial lithium products are available because of lithium's electrochemical reaction and other unique properties. Lithium is sold as brines, compounds, metal, or mineral concentrates depending on the end use. Most lithium compounds and minerals are consumed in the production of ceramics, glass, and primary aluminum. The use of organic lithium compounds as industrial catalysts and the consumption of various lithium compounds in lithium

batteries are the most rapidly expanding markets. General reviews are available (3–5).

2. Occurrence

Lithium is widely distributed in nature. Trace amounts are present in many minerals, in most rocks and soils, and in many natural waters. The lithium content of the earth's crust is estimated to be from 20 to 70 ppm by weight. This compares with the more familiar lead constituent, estimated at only 16 ppm of the earth's crust, and zinc at 1 ppm. Ocean water contains about 0.18 ppm Li, whereas many natural brines have several hundred ppm and a few brines contain more than 1000 ppm Li. Typical values for igneous rocks range from 35 ppm for granites to less than 1 ppm for ultramafic rocks. Lithium does not readily substitute for calcium or magnesium in carbonate rocks; thus lithium content in limestones and dolomites is low, typically about 8 ppm. Lithium is contained mostly in the accessory minerals, especially in clays (qv). The typical lithium content of shales and clays is about 70 ppm, although some clays and clay minerals contain from several hundred to 5000 ppm Li. In geochemical behavior, lithium differs from the other alkali metals. It forms no feldspar structure and shows very limited ability to substitute for sodium and potassium in feldspars. Rather, lithium shows a marked tendency to substitute for Mg^{2+} and Fe^{2+} . Thus, in igneous rocks, the lithium that is present generally is concentrated in the dark ferromagnesian minerals such as biotite, amphiboles, and pyroxenes (see ASBESTOS).

Lithium-bearing minerals occur mainly in granitic pegmatites, which are coarse-grained igneous rocks composed largely of quartz, feldspar, and mica. Accessory minerals often are present in these pegmatites that contain less abundant elements, such as lithium, tin, and beryllium. Only spodumene [1302-37-0], $\text{LiAlSi}_2\text{O}_6$, and petalite [1302-66-5], $\text{LiAlSi}_4\text{O}_{10}$, are important lithium sources from minerals. Lithium also is present in some sedimentary deposits or in brines associated with granitic pegmatites. It is possible that the concentrations resulted from the extraction of lithium from igneous rocks or volcanic ash by hydrothermal action, with the eventual formation of lithium minerals in the sediments or lithium concentrations in the associated brines. The latter hypothesis is in agreement with the cation-exchange properties of lithium and the high solubility of lithium salts.

2.1. Ore Minerals and Deposits. Spodumene, a lithium aluminum silicate, $\text{LiAlSi}_2\text{O}_6$, has a theoretical lithia [12057-24-8], Li_2O , content of 8.03%. It is the most important lithium ore mineral and is characterized by high lithium content, extensive deposits, and processing advantages. It is the principal mineral source for the production of lithium chemicals and, as beneficiated mined ore, it is an important source of lithium in ores used directly in the glass and ceramics (qv) industry. Run of mine ore generally contains 1–2% Li_2O with some deposits giving concentration as high as 4.0%. Concentration to 5–6% is necessary for lithium extraction. Ores for sale are beneficiated to 4.8% for bulk container glass usage and as high as 7.6% for use in tableware, ceramics, frits, and glazes (6). Concentration of run of mine ore is achieved by froth flotation (qv)

of the spodumene away from feldspathic sands and other tailings. Natural spodumene is a monoclinic pyroxene having a density of 3.16 g/cm^3 . On heating to about $1000\text{--}1100^\circ\text{C}$, natural α -spodumene undergoes an irreversible phase change to the tetragonal β -spodumene, density 2.400 g/cm^3 . The open lattice of β -spodumene is much more amenable to chemical attack than is α -spodumene. In North America, principal deposits are in North Carolina, Quebec, Manitoba, and the Northwest Territories. The most extensive deposit worldwide is in Australia. Other deposits are in Brazil, the CIS, People's Republic of China, and Zaire (see MINERAL RECOVERY AND PROCESSING).

Petalite, also a monoclinic lithium aluminum silicate, $\text{LiAlSi}_4\text{O}_{10}$, has a theoretical Li_2O content of 4.88%. Commercial ores usually contain 3.5–4.5% Li_2O without concentration and are a preferred source of lithia for use in ceramics and specialty glazes. Petalite is monoclinic and has a density of $2.4\text{--}2.5 \text{ g/cm}^3$. Heating to high temperature results in an irreversible phase change to a β -spodumene– SiO_2 solid solution that could provide an extractable source for the production of lithium chemicals. Large deposits of petalite occur at Bikita in southern Zimbabwe, Namibia, Brazil, Australia, and the CIS.

Lepidolite [1317-64-2] and amblygonite [1302-58-5] have selective use in supplying lithia to special glasses, ceramics, and glazes by direct addition of the ore. These are not, however, used for the manufacture of lithium chemicals. Lepidolite is a complex lithium mica of variable composition. Li_2O content is from 3–4%. One formula is $\text{K}(\text{Li},\text{Al})_3(\text{Si},\text{Al})_4\text{O}_{10}(\text{F},\text{OH})_2$. Rubidium and cesium are usually present in lepidolite, which is an ore source for rubidium (see RUBIDIUM AND RUBIDIUM COMPOUNDS). Commercial grades of amblygonite, $\text{Li}(\text{F},\text{OH})\text{AlPO}_4$, contain 8.0% Li_2O and 20% P_2O_5 and act as a source of fluorine as well as lithium. A commercial grade of 7.0% Li_2 and 8% P_2O_5 is also available (7).

2.2. Brine Sources. Lithium occurs naturally in brines from salars, saline lakes and seawater, oil-field waters, and geothermal brines. Of these sources, lithium is produced only from brines of two salars.

Salars and Lakes. Brines having high lithium concentration are found in salars of northern Chile, southwestern Bolivia, and northwestern Argentina. Brines of lower lithium concentration are found in salars in the western United States and the Tibetan Plateau. Brines pumped from beneath the surface of the Salar de Atacama (Chile) and Silver Peak (Clayton Valley, Nevada) are used for commercial production of lithium utilizing solar evaporation (see CHEMICALS FROM BRINES). The concentration of selected ions in brines from salars and lakes of potential commercial interest worldwide are shown in Table 1.

The salars, or playas, in South America are dried lake beds within a closed or restricted drainage basin. These are normally composed of a salt crust that is interspersed with varying amounts of sands, clays, and other detritus. The largest constituent of the evaporite in these deposits is sodium chloride. Whereas these salars may have been sea-filled at one time, the mineral contents are not marine in origin, but come from other primary source material, such as erosion of surrounding hills, or from volcanic or other underground activity. The salt crust is usually porous, more so near the surface, and the interstices contain the salt brines. South American salars are at high elevations, from 2300–3600 m. The largest, Uyuni, covers approximately 9000 km^2 .

Oil Fields. Oil field waters in the United States containing lithium have been identified in 10 states. The greatest concentrations are in waters from the Smackover formation of southern Arkansas and eastern Texas. Concentrations from this formation have been measured from 300–600 ppm in waters originating at a 2500–3300 m depth. Recovery of lithium from this resource would only be commercially feasible if a selective extraction technique could be developed. Lithium as a by-product of the recovery of petroleum (qv), bromine (qv), or other chemicals remains to be exploited (12).

Geothermal Sources. Geothermal brines in the United States containing lithium from 55–238 ppm occur near the Salton Sea in southern California in fluids obtained at a depth of about 1500 m. Lower concentrations of lithium occur in other geothermal brines in the Pacific rim countries. Recovery of lithium from geothermal brines would be secondary to the intent of the development of geothermal resources, namely, power generation (qv) and production of fresh water (GEOTHERMAL ENERGY) (13).

2.3. Clays and Other Sources. Sedimentary deposits, especially lithium-bearing clays found in the western United States, offer an additional source of lithium. These clays contain lithium-bearing trioctahedral smectites, of which hectorite [12173-47-6], $\text{Na}_{0.33}(\text{Mg},\text{Li})_3\text{Si}_4\text{O}_{10}(\text{F},\text{OH})_2$, is one mineral. Hectorite usually contains 0.3–0.6% Li or 0.7–1.3% Li_2O . Deposits are found in Nevada, California, Utah, Oregon, Wyoming, Arizona, and New Mexico. The most significant deposits are in southern Nevada, in the Lake Mead area, and in the McDermitt caldera complex on the Nevada–Oregon border. In the McDermitt caldera, lithium probably originated from volcanic sedimentary rocks deposited in the caldera moat. There is evidence that areas of the caldera were hydrothermically active contributing to enrichment of lithium (14). This and other similar deposits are not economically viable as of this writing. These deposits do represent a significant lithium reserve, however, whenever large expansion in demand occurs.

Flint clays and other related rocks are another potential lithium source. These are high alumina clays that are composed largely of well-crystallized kaolinite [1318-74-1] and are used for the manufacture of refractories (qv). The lithium content ranges from <100 to 5000 ppm. Deposits occur in many states, including Missouri, Pennsylvania, and Ohio. Lithium (at ca 1.3%) is present in a chlorite mineral that is similar to cookeite [1302-92-7]. High lithium contents may be the reason why some deposits are unsatisfactory for refractory use.

2.4. World Reserves and Resources. A summary of worldwide production, reserves and reserve base of lithium is given in Table 2 (15).

3. Recovery

3.1. Recovery from Ores and Clays. The preferred method of extraction of lithium from spodumene ore is the sulfuric acid process (16), used on ore concentrates of 5–6% Li_2O , representing 62–74% pure spodumene. Methods suitable for extraction from spodumene also can be used for petalite, because the latter mineral converts to β -spodumene– SiO_2 solid solution on heating to a high temperature.

Sulfuric Acid Process. Natural α -spodumene is virtually unattacked by hot sulfuric acid; thus the first step in the extraction process is the conversion of α -spodumene to the much more reactive β -spodumene by heating to 1075–1100°C in a brick-lined rotary kiln. Although the melting point of β -spodumene is greater than 1400°C, the maximum ore temperature that is reached must be well below 1400°C, otherwise, the gangue minerals present in the ore concentrate could form low melting mixtures with spodumene. The kiln discharge is cooled, ground by ball milling to $<149\ \mu\text{m}$ (-100 mesh), and mixed with 93% (66°Bé) sulfuric acid (density 1.84) in an amount equivalent to the lithium present plus about 35% excess. The mixture is roasted in a small rotary kiln to about 250°C. An exothermic reaction results, starting at about 175°C, in which hydrogen ions from the acid replace lithium ions in the β -spodumene structure to form soluble lithium sulfate [10377-48-7], leaving an insoluble ore residue.

The kiln discharge is leached with water, resulting in an impure lithium sulfate solution that contains the excess sulfuric acid and small amounts of aluminum, iron, and other alkali sulfates. The excess sulfuric acid is neutralized with ground limestone. The slurry is then filtered to separate the ore residue, giving a mixed alkali sulfate solution that is free of iron and aluminum but that is saturated with calcium sulfate. The solution also contains magnesium ions derived mainly from the limestone. Magnesium is precipitated using hydrated lime, followed by precipitation of calcium using soda ash or mother liquor containing sodium carbonate generated in subsequent precipitation of by-product sodium sulfate decahydrate. After filtration, the solution is adjusted using sulfuric acid to pH 7–8, followed by concentration in a multiple-effect evaporator to alkali sulfate concentration of 350 g/L, 200–250 g/L of this being lithium sulfate. After a clarifying filtration, lithium carbonate is precipitated at 90–100°C with a 28 wt% soda ash solution. The precipitated lithium carbonate is centrifuged, washed, and dried. Approximately 15% of the lithium remains in the mother liquor, along with residual sodium carbonate and large amounts of sodium sulfate. Cooling to about 0°C separates the greater part of the sodium sulfate as the decahydrate, which is centrifuged and converted to the anhydrous salt for by-product sale. The mother liquor from the sodium sulfate decahydrate precipitation is recycled for lithium and soda ash values.

Other Recovery Processes. Most other processes that have been described for the extraction of lithium can be classified as being either alkaline or ion-exchange (qv). The alkaline methods (17,18) are based on the reaction of the ore with limestone at high temperature in a rotary kiln, sometimes with the addition of salt such as a calcium sulfate or calcium chloride. Sintering occurs in these reactions and it is necessary to grind resulting clinkers prior to leaching. Water leaching following the reaction of ore and limestone alone yields an impure lithium hydroxide solution, whereas the use of additives results in lithium sulfate or chloride solutions. The required high weight ratio of limestone to ore, often nearly 4:1, is a disadvantage as is the necessity of grinding the clinker prior to leaching.

A great number and variety of methods comprise the ion-exchange group. These methods involve heating the ore, usually β -spodumene and generally at relatively moderate temperatures, in contact with the desired reagent, which is either an acid or an alkali metal salt. The latter may be either fused

or in aqueous solution. Ion exchange occurs. The lithium ions in the ore are replaced by hydrogen, sodium, or potassium ions, thus forming the soluble lithium salt of the anion that was used.

One ion-exchange process, which was used for several years by Quebec Lithium Corp., is based on the reaction of β -spodumene with an aqueous sodium carbonate solution in an autoclave at 190–250°C (19). A slurry of lithium carbonate and ore residue results, and is cooled and treated with carbon dioxide to solubilize the lithium carbonate as the bicarbonate. The ore residue is separated by filtration. The filtrate is heated to drive off carbon dioxide resulting in the precipitation of the normal carbonate.

Another ion-exchange method involves contacting β -spodumene with a strongly acidic cationic-exchange resin in the presence of water at 90–150°C and subsequently separating the resin and eluting the lithium values (20). In another process, β -spodumene reacts with a sodium chloride or sodium sulfate solution in an autoclave at 100–300°C to form the corresponding lithium salt in the solution (21). In another ion-exchange process, β -spodumene reacts with fused sodium or potassium acetate; double the amount of salt equivalent to the amount of lithium in ore is used (22). The mixture is heated slowly to 324°C, cooled, the reaction mass ground, and lithium acetate leached countercurrently with hot water. Lithium carbonate is precipitated from the acetate solution by hot concentrated soda ash. Sodium acetate is recovered from the mother liquor and recycled.

3.2. Recovery from Clays. Limestone–gypsum roasting and selective chlorination have been demonstrated to be applicable to extracting lithium from clays containing hectorite. However, chlorination techniques do not give lithium extraction recovery above 20% (23). With these processes, lithium silicate in the clay is converted to either water-soluble lithium sulfate or chloride. The limestone–gypsum roast-water leach process (24) is similar to the alkaline roast process for ores. In this process a mixture of clay, limestone, and gypsum is pelletized, dried, and fed to a roasting furnace where lithium in the clay converts at 900°C to water-soluble lithium sulfate. Water leaching of the calcine produces a mixed alkali sulfate and a small amount of calcium sulfate. This solution, together with recycle streams, is concentrated by evaporation. Calcium precipitates as the carbonate and is filtered. Lithium carbonate is precipitated by soda ash addition. The mother liquor from this precipitation is cooled to crystallize glazerite and glauber's salt that is separated. This liquor is recycled for recovery of the lithium values. Lithium recovery in excess of 80% has been demonstrated.

3.3. Recovery from Brines. Natural lithium brines are predominately chloride brines varying widely in composition. The economical recovery of lithium from such sources depends not only on the lithium content but on the concentration of interfering ions, especially calcium and magnesium. If the magnesium content is low, its removal by lime precipitation is feasible. Location and availability of solar evaporation (qv) are also important factors.

The Salar de Atacama in the Chilean Andes is the largest commercial source for lithium from brines. Brines of 0.15% lithium, 28% total dissolved solids, are pumped from 30-m deep wells into a series of solar evaporation ponds where concentration is increased and composition altered (25). High solar evaporation rates are achieved owing to strong solar radiation, low humidity,

moderately intense winds, and low (25-mm/yr) average rainfall. Freshwater evaporation rates are about 3000 mm/yr (26). In processing, a calcium chloride brine is added, causing precipitation of the sulfate ion as gypsum. Magnesium, sodium, and potassium precipitate as halite, sylvanite, carnallite, and bischofite (27). To maintain brine volume in the ponds, precipitated salts are harvested regularly. More concentrated lithium-containing brines are recovered from precipitated salts by use of thickeners and centrifugation. Lithium concentration of 4–6% is attained in the produced chloride brine, which contains some residual borate and magnesium. Prior to precipitating lithium carbonate, borate is removed by extraction. Magnesium is then removed by two-stage precipitation, using sodium carbonate and lime, respectively. The purified brine is reacted with saturated soda ash solution to precipitate lithium carbonate. Even though the magnesium content of the brines from the Atacama is 6.4 times greater than the lithium content, the lithium concentration is the highest known. This is a very economical operation, partly because of the favorable conditions for solar evaporation and despite the remote location of the salar.

Lithium is also produced from brines at Clayton Valley, Nevada, where lithium is only present at 0.03% in brines pumped from wells of 90–210 m. Magnesium content of this brine is low (0.04%) allowing removal by precipitation with lime. Lime is added in the fourth of nine ponds, raising the pH to 11 and causing hydrated magnesia and gypsum to precipitate. Most of the remaining calcium precipitates in subsequent ponds owing to carbon dioxide absorption. Solar evaporation increases concentrations to saturation and precipitation of sodium chloride and other salts follows. The lithium concentration increases to 0.5%. The resultant brines from the evaporation ponds are then treated with lime and soda ash to remove remaining magnesium and calcium prior to reaction with saturated soda ash solution to precipitate lithium carbonate (28).

The Clayton Valley brine contrasts with other lithium-bearing brines which often contain higher magnesium content. Brine of the Great Salt Lake, for example, contains 0.006% lithium and 0.8% magnesium. Magnesium removal with lime is not feasible because of high reagent cost and the sheer volume of a magnesium precipitate. Instead, lithium chloride would need to be selectively removed from the brine. Various ion-exchange and liquid–liquid extraction methods have been suggested but these methods are not used commercially. In one proposed procedure, lithium chloride is converted to lithium tetrachloroferrate [15274-95-0] and is extracted using a water-insoluble organic solvent (29). Another approach involves precipitation of a lithium aluminate from the brine by adding freshly precipitated aluminum hydroxide or by adding aluminum chloride followed by pH adjustment (30). This method is also suggested for use in recovery of lithium from geothermal brines (31).

The lithium-bearing oil-field waters of southern Arkansas and eastern Texas contain high concentrations of calcium chloride. The application of ion-exchange technology has been proposed where lithium is selectively absorbed from brines high in calcium and sodium, and then recovered through regeneration using an aqueous solution of low lithium concentration. Ion adsorption resins for this application are prepared by forming crystalline $\text{LiOH} \cdot 2\text{Al}(\text{OH})_3 \cdot n\text{H}_2\text{O}$ by reaction of $\text{Al}(\text{OH})_3$ suspended in the resin with aqueous LiOH at elevated temperatures. The crystalline $\text{LiOH} \cdot 2\text{Al}(\text{OH})_3$ thus formed

can be beneficially converted to $\text{LiX} \cdot 2\text{Al}(\text{OH})_3$, where X is a halide. These lithium aluminates are useful in selectively recovering lithium ions from solution if the amount of lithium in the aluminate structure is first reduced to a lower concentration, but not completely removed, leaving space in the crystal for taking up a lithium salt until the crystal is again loaded with that salt (32).

4. Properties

Lithium [7439-93-2], an alkali metal, has a silvery luster, an atomic number of 3, an atomic weight of 6.941, and a $1s^2 2s^1$ electronic configuration. It is the first metallic member of Group 1 (IA) in the Periodic Table and is preceded only by hydrogen and helium. Two stable isotopes are present in natural lithium: ^7Li having an abundance of 92.4 at. % and ^6Li , 7.6 at. %. Lithium, density = 0.531g/cm^3 at 20°C , is the lightest of all solid elements. In general, the properties of lithium are similar to those of the other alkali metals, eg, ease of oxidation to form a univalent ion, the strongly basic property of the hydroxide, etc. In the alkali metal group, lithium has the highest melting point, boiling point, and heat capacity, and the smallest ionic radius, ie, 60 pm. The ionic radius and the resulting high ionic charge density largely account for the unusual properties and effects of lithium such as the powerful fluxing action of lithia [12057-24-8], Li_2O , in ceramic compositions. It remains untarnished in dry air but in moist air, its surface becomes coated with a mixture of LiOH [1310-65-2], $\text{LiOH} \cdot \text{H}_2\text{O}$ [1310-66-3], Li_2CO_3 [554-13-2], and Li_3N [26134-62-3] (33).

Thin films (qv) of lithium metal are opaque to visible light but are transparent to uv radiation. Lithium is the hardest of all the alkali metals and has a Mohs' scale hardness of 0.6. Its ductility is about the same as that of lead. Lithium has a bcc crystalline structure which is stable from about -195 to -180°C . Two allotropic transformations exist at low temperatures: bcc to fcc at -133°C and bcc to hexagonal close-packed at -199°C (34). Physical properties of lithium are listed in Table 3.

The reaction of hydrogen and lithium readily gives lithium hydride [7580-67-8], LiH , which is stable at temperatures from the melting point up to 800°C . Lithium reacts with nitrogen, even at ordinary temperatures, to form the reddish brown nitride, Li_3N . Lithium burns when heated in oxygen to form the white oxide, Li_2O .

Lithium reacts with water, evolving hydrogen, but does not ignite unless the metal is finely divided. In this respect, it is less reactive than other alkali metals. Lithium amide [7782-89-01], LiNH_2 , is formed by reaction with ammonia. This direct synthesis is not used for manufacture of commercial quantities, however, because of the difficulties of temperature control and competing alternative reactions. Carbon dioxide reacts with lithium only at high temperatures. Halogens react readily with lithium with consequent emission of light (42). In general, lithium reacts violently with inorganic acids, although it reacts slowly with cold sulfuric acid.

Like the other alkali metals (43), lithium has appreciable solubility in liquid ammonia. A saturated solution at -33.2°C contains 15.7 mol lithium in 1000 g of ammonia, and at 19°C has a density of 0.477, lower than that of any other known

liquid. Lithium reacts readily in liquid ammonia to form compounds, eg, lithium sulfide [12136-58-2], Li_2S ; lithium selenide [12136-60-6], Li_2Se ; and the mono- [1111-64-4] and diacetylide [1070-75-3]. Lithium reacts with many organic halides to form organolithium compounds (44), and with carbon to form lithium carbide [1070-75-3], Li_2C_2 , at temperatures above 800°C (45).

5. Manufacture

An electrolytic process devised in 1893 (46) resembles the one generally used for lithium production. Molten salt electrolysis from a lithium chloride–potassium chloride mixture is performed using graphitized carbon rod as the anode and a carbon steel cell body as the cathode. Modern U.S. installations employ a 55 wt% LiCl –45 wt% KCl electrolyte at about 460°C . Two grades are produced by electrolysis. The essential difference is in sodium concentration. Metal having about 0.6% sodium is used as a reactant in synthesizing inorganic derivatives, organolithiums, and other organic intermediates. Metal having 100 ppm sodium is used for manufacture of high energy batteries and for alloying with other metals. Sodium concentration is determined by sodium in the LiCl feed, which reports stoichiometrically to the metal. Metallic impurities are less than 100 ppm. Contamination by oxygen and nitrogen is controlled by minimizing the exposure of the liquid metal to the atmosphere and by keeping the cell temperature as low as possible. Cells are fabricated of steels of 0.25–0.3% carbon or of low carbon steels. Low carbon steels are more resistant to decarbonization from the produced lithium, although they are less forgiving of excessive temperatures. Typical current efficiency is 80–85% and lithium recovery is $>98\%$ based on charged chloride.

Lithium metal can also be produced by electrolysis in nonprotic solvents. Other methods based on reduction by metals, eg, aluminum or silicon from the chloride or by magnesium from the oxide, have not had practical commercial application.

6. Shipment

Lithium metal, UN No. 1415, is classified by the United States Department of Transportation as “Dangerous When Wet.” The required shipping label which shows this classification identifies the key hazards: emission of flammable gases on reaction with water, corrosivity to eyes and skin, and solid flammability. Lithium does not need the same degree of stringent safety precautions as do the other alkali metals because it does not burn spontaneously upon reaction with water. However, lithium can ignite when its surface films dissolve or if heated, with resulting vigorous fires; hence, contact with moisture should be avoided. Lithium can be handled easily at temperatures up to 225°C in argon, helium, or carbon dioxide.

Liquid lithium is easily ignited in air and, once it has begun to burn, requires special techniques to extinguish. Dry-powdered lithium chloride is an effective extinguisher. Copper powder (Navy 125F sold by The Ansul Co. and

others) has UL approval as an extinguishing agent for lithium fires. Another material, LITH-X (The Ansul Co.), is a compound of a special graphite base that extinguishes lithium fires by excluding air and conducting heat away from the burning mass. Water, sand, carbon tetrachloride, and carbon dioxide cannot be used. Lithium is usually stored under mineral oil, or with an oil coating to passivate the surface, in metal drums. If the drum is not airtight, a slow deterioration of the surface occurs and lithium nitride [26134-62-3] forms. Under airtight conditions, lithium can be stored indefinitely.

7. Economic Aspects

The total lithium compounds market was estimated to be 45,000 t in 2001 (47). Global consumption was estimated to be 158,000 t in 2000 (48).

The health of the domestic lithium industry remains closely tied to the performance of the aluminum and glass and ceramics industries in the United States. In 2001, U.S. aluminum capacity was idle and lithium demand suffered. Demand for lithium for batteries and alloys is expected to increase, but total consumption of metal will remain low compared to lithium compounds.

Lithium-ion and lithium-polymer batteries appear to possess the greatest growth potential. Market for rechargeable batteries grew to $\$3 \times 10^9$ in 1998 and should reach $\$6 \times 10^9$ by 2005. No reliable forecasts have been made to predict the use of lithium in hybrid vehicles.

Table 4 gives salient statistics for the U.S. (15). Table 5 gives U.S. import data and Table 6 gives export data for lithium compounds (49).

8. Specifications

Lithium metal is available commercially in ingots, special shapes, shot, and dispersions. Ingots are sold in 0.11-, 0.23-, 0.45-, and 0.91-kg sizes. Special shapes include foil, wire, and rod. Lithium is available in hermetically sealed copper cartridges and in sealed copper tubes for use in treating molten copper and copper-base alloys. Shot is sold in 1.19–4.76 mm (16–4 mesh) sizes. Lithium dispersions (30% in mineral oil) of 10–50- μ m particle size are used primarily in organic chemical reactions. Dispersions in other solvents and of other size fraction and be supplied.

9. Analytical Methods

Lithium can be detected by the strong orange-red emission of light in a flame. Emission spectroscopy allows very accurate determination of lithium and is the most commonly used analytical procedure. The red emission line at 670.8 nm is usually used for analytical determinations although the orange emission line at 610.3 nm is also strong. Numerous other methods for lithium determinations have been reviewed (50,51).

10. Health and Safety Factors

10.1. Handling. Lithium is a very dangerous fire hazard when exposed to heat or flame. The powder may ignite spontaneously in air. The solid metal ignites above 180°C. Most types of fire extinguishers may cause an explosion. Special mixtures of dry chemicals, soda ash, and graphite should be used. Molten lithium is extremely reactive and attacks otherwise inert materials such as sand, concrete, and ceramics.

10.2. Toxicity. Lithium oxides, hydroxide, and carbonate are strong bases and their water solutions are very caustic. The toxicity of lithium compounds is a function of their solubility in water. Lithium ion is toxic to the central nervous system. Lithium ion is commonly ingested at dosages of 0.5 g/d of lithium carbonate for treatment of bipolar disorders. Therapeutic levels versus toxic levels are small: 2 mmol/L is toxic; 4 mmol/L is fatal. Lithium hydroxide, either directly or formed by the hydrolysis of other salts, can cause caustic burns. Skin contact with lithium halides can result in skin dehydration. In industry the most hazardous lithium compound is the hydride (52). Organo-lithium compounds are often pyrophoric and require special handling.

Some effects of lithium exposure are tremors, nausea, slurred speech, vertigo, and thirst. Continued exposure effects include apathy, anorexia, fatigue, and muscle weakness. Long term effects include memory impairment, edema, weight gain, kidney damage, coma, and cardiac arrhythmia. Aplastic anemia is possible (52).

11. Uses

The largest use of lithium metal is in the production of organometallic alkyl and aryl lithium compounds by reactions of lithium dispersions with the corresponding organohalides. Lithium metal is also used in organic syntheses for preparations of alkoxides and organosilanes, as well as for reductions. Other uses for the metal include fabricated lithium battery components and manufacture of lithium alloys. It is also used for production of lithium hydride and lithium nitride.

The use of lithium compounds in ceramics, glass, and primary aluminum production represented more than 60% of estimated domestic consumption. Other major end uses for lithium were in the manufacture of lubricants and greases and in the production of synthetic rubber.

11.1. Metallurgy. Lithium forms alloys with numerous metals. Early uses of lithium alloys were made in Germany with the production of the lead alloy, Bahnmetall (0.04% Li), which was used for bearings for railroad cars, and the aluminum alloy, Scleron. In the United States, the aluminum alloy X-2020 (4.5% Cu, 1.1% Li, 0.5% Mn, 0.2% Cd, balance Al) was introduced in 1957 for structural components of naval aircraft. The lower density and structural strength enhancement of aluminum lithium alloys compared to normal aluminum alloys make it attractive for uses in airframes. A distinct lithium–aluminum phase (Al_3Li) forms in the alloy which bonds tightly to the host aluminum matrix to yield about a 10% increase in the modulus of elasticity of the

aluminum lithium alloys produced by the main aluminum producers. The density of the alloys is about 10% less than that of other structural aluminum alloys.

Lithium magnesium alloys, developed during World War II, have found uses in aerospace applications. Lithium alters the crystallization of the host magnesium from the normal hexagonal structure to the body-centered cubic structure, with resultant significant decreases in density and increases in ductibility.

Aircraft manufacturers in several countries have considered using aluminum–lithium alloys for wing and fuselage skin or for structural members in different types of aircraft. Use of these alloys could reduce the weight of the aircraft by more than 10%, allowing significant fuel savings during the life of the aircraft. The alloys, which are 2% to 3% lithium by weight, were attractive to the aircraft and aerospace industries because of their reduced density and improved corrosion resistance compared with conventional aluminum alloys. These alloys, however, have not been as widely used in aircraft manufacture as a result of direct competition from composite materials (54).

The superlightweight external fuel tank for the National Aeronautics and Space Administration's Space Shuttle was made with another aluminum alloy containing 4% copper, 1% lithium, 0.4% silver, 0.4% magnesium, and the remainder aluminum. This alloy was 30% stronger and 5% less dense than the more traditional aluminum alloy that it replaced. The redesigned fuel tank weighed about 3,400 kilograms less than the original design; the weight savings were used to increase the payload capacity of shuttle missions (54).

Lithium is used in metallurgical operations for degassing and impurity removal (see METALLURGY). In copper (qv) refining, lithium metal reacts with hydrogen to form lithium hydride which subsequently reacts, along with further lithium metal, with cuprous oxide to form copper and lithium hydroxide and lithium oxide. The lithium salts are then removed from the surface of the molten copper.

11.2. Electrochemical Applications. Lithium batteries (qv) are used in numerous consumer, medical, industrial, and military applications. The advantages of lithium batteries include not only the light weight and high energy density, but also short voltage delays and low self-discharge rates. Consumer uses include uses in electronic devices such as watches, cameras, and calculators as well as CMOS-RAM memory backups. Lithium batteries are especially adaptable to unusual configurations and miniaturization, which make them especially useful in small electronics. Medical uses include cardiac pacemakers. Industrial uses include power for remote sensing devices such as oil-well logging devices. Lithium batteries have uses in military applications ranging from communication devices to stand-by power for missile systems.

Most primary lithium batteries contain a lithium anode, although use of lithium alloys, especially Li–Al alloys, is preferred in many applications requiring higher temperatures. Most cathode materials are lithium intercalation compounds such as metal oxides or sulfides, although carbon monofluoride, CF_x , and liquid cathode materials such as thionyl chloride [7719-09-7], SOCl_2 , and sulfur dioxide [7446-09-5], SO_2 , are also extensively used. The electrolytes are usually a lithium salt dissolved in an organic electrolyte, although lithium ion-conductive solids and glasses are used in many applications. Common electrolyte salts are

lithium bromide [7550-35-8], LiBr; lithium hexafluoroarsenate [29935-35-1], LiAsF₆; lithium hexafluorophosphate [21324-40-3], LiPF₆; lithium iodide [10377-51-2], LiI; lithium perchlorate [7791-03-9], LiClO₄; lithium tetrachloroaluminate [14024-11-4], LiAlCl₄; lithium tetrafluoroborate [14283-07-9], LiBF₄; and lithium trifluoromethane sulfonate [33454-82-9] (triflate), LiCF₃SO₂, which are soluble in a variety of organic solvents and are not easily reduced by lithium. Lithium reaction with the solvent or the electrolyte salt is prevented by formation of a thin lithium ion-conductive film at the lithium–electrolyte interface, formed by reaction of lithium with either the solvent or the salt.

The attractiveness of lithium rechargeable (secondary) batteries has long been recognized. The high energy density, light weight, and other performance and environmental factors make secondary lithium batteries desirable for applications ranging from portable electronic devices to power supply for traction vehicles. The first attempts to commercialize secondary lithium batteries employed lithium metal anodes, which have largely been discontinued owing to safety hazards resulting in fires, especially under abuse conditions. Polymeric lithium ion-conductive electrolytes are one method of preventing the occurrence of this problem. The low conductivity of current polymeric electrolytes such as LiPF₆ in poly(ethylene oxide) require use of high surface area, thin-film lithium in order to achieve satisfactory performance. Another method of preventing this problem has been to use lithium ion intercalation compounds for both the anode and the cathode. Such batteries are known as lithium ion or “rocking chair” batteries (49) because the lithium ion swings between intercalation compounds at the anode and cathode during the charge and discharge cycles.

Electric vehicles (EVs) have been considered a large potential market for lithium batteries, but general acceptance of these vehicles has been slow. Hybrid vehicles and vehicles powered by fuel cells may find greater popularity in the near future than pure EVs.

Nonrechargeable (primary) lithium batteries offer improved performance compared with alkaline batteries at a slightly higher cost and have been commercially available for more than 10 years. They are used in cameras, electronic games, microcomputers, small appliances, toys, and watches. The military purchased large and small lithium batteries for a variety of military applications. For example, in 2000, two lithium oxyhalide reserve batteries were qualified for use in two different missile programs, the High Altitude Area Defense Program and the Boeing Ground Based Program. These reserve batteries, which are stored in an inactive form until needed for short-term use, provide high current for short times from small packages (55).

12. Inorganic Lithium Compounds

The unique properties of the lithium ion result in part from its small size and correspondingly high charge density. The ⁶Li isotope which has a large neutron capture radius finds uses in thermonuclear devices, neutron shielding, and tritium production. All of these are especially important for the fusion reactors proposed for future power generation (see FUSION ENERGY). Lithium is also used for treating affective mood disorders and has been proposed for other medical

applications (see PSYCHOPHARMACOLOGICAL AGENTS) (53). The size and charge density of this lightest metal ion are expected to lead to additional uses in emerging technologies.

12.1. Lithium Acetate. Lithium acetate [546-89-4] is obtained from reaction of lithium carbonate or lithium hydroxide and acetic acid. Crystalline lithium acetate dihydrate [6108-17-4], $\text{CH}_3\text{CO}_2\text{Li} \cdot 2\text{H}_2\text{O}$, melts congruently in its own water of crystallization at 57.8°C . The anhydrous salt [546-89-4] melts without decomposition at 291°C . Aqueous solubility, expressed as the anhydrous salt, is 31% at 25°C and 66% at 100°C . Uses of lithium acetate are in polyester fiber (see FIBERS, POLYESTER) manufacture and in certain catalytic processes.

12.2. Lithium Amide. Lithium amide [7782-89-0], LiNH_2 , is produced from the reaction of anhydrous ammonia and lithium hydride. The compound can also be prepared by the removal of ammonia from solutions of lithium metal in the presence of catalysts (56). Lithium amide starts to decompose at 320°C and melts at 375°C . Decomposition of the amide above 400°C results first in lithium imide, Li_2NH , and eventually in lithium nitride, Li_3N . Lithium amide is used in the production of antioxidants (qv) and antihistamines (see HISTAMINE AND HISTAMINE ANTAGONISTS).

12.3. Lithium Benzoate. Lithium benzoate [553-54-8], $\text{LiC}_7\text{H}_5\text{O}_2$, is formed by reaction of benzoic acid and lithium hydroxide in aqueous solution with subsequent drying. The salt is very soluble (29.9 g/100 g soln at 25°C) in water. It is used as an alkaline catalyst for curing epoxides and as a crystal nucleation modifier in polypropylene.

12.4. Lithium Borates. Lithium metaborate [13453-69-5], $\text{LiBO}_2 \cdot 2\text{H}_2\text{O}$, is prepared from reaction of lithium hydroxide and boric acid. It is used as the fluxing agent for the matrix for x-ray fluorescence analytical techniques and in specialty glasses and enamels. The anhydrous salt melts at 847°C .

Lithium tetraborate [1303-94-2], $\text{Li}_2\text{B}_4\text{O}_7$, is used as a flux in ceramics and in x-ray fluorescence spectroscopy. The salt has also been proposed for nonlinear optic applications. The salt melts at 917°C (see NONLINEAR OPTICAL MATERIALS).

12.5. Lithium Carbonate. Lithium carbonate [554-13-2], Li_2CO_3 , is produced in industrial processes from the reaction of sodium carbonate and lithium sulfate or lithium chloride solutions. The reaction is usually performed at higher temperatures because aqueous lithium carbonate solubility decreases with increasing temperatures. The solubility (wt%) is 1.52% at 0°C , 1.31% at 20°C , 1.16% at 40°C , 1.00% at 60°C , 0.84% at 80°C , and 0.71% at 100°C . Lithium carbonate is the starting material for reactions to produce many other lithium salts, including the hydroxide. Decomposition of the carbonate occurs above the 726°C melting point. A method for the production of low sodium lithium carbonate from brines has been disclosed (57).

Lithium carbonate addition to Hall-Heroult aluminum cell electrolyte lowers the melting point of the eutectic electrolyte. The lower operating temperatures decrease the solubility of elemental metals in the melt, allowing higher current efficiencies and lower energy consumption (49). The presence of lithium also decreases the vapor pressure of fluoride salts.

Lithium carbonate is used to prepare lithium aluminosilicate glass ceramics which have low thermal coefficients of expansion, allowing use over a wide temperature range. It also finds uses in specialty glasses and enamels.

The molten carbonate fuel cell uses eutectic blends of lithium and potassium carbonates as the electrolyte. A special grade of lithium carbonate is used in treatment of affective mental (mood) disorders, including clinical depression and bipolar disorders. Lithium has also been evaluated in treatment of schizophrenia, schizoaffective disorders, alcoholism, and periodic aggressive behavior (58).

12.6. Lithium Halides. Lithium halide stability decreases with increasing atomic weight of the halogen atom. Hence, the solubility increases from the sparingly soluble lithium fluoride to the very soluble bromide and iodide salts. The low melting points of lithium halides are advantageous for fluxes in many applications.

Lithium Fluoride. Lithium fluoride [7789-24-4], LiF, is a white nonhygroscopic crystalline material that does not form a hydrate. The properties of lithium fluoride are similar to the alkaline-earth fluorides. The solubility in water is quite low and chemical reactivity is low, similar to that of calcium fluoride and magnesium fluoride. Several chemical and physical properties of lithium fluoride are listed in Table 7. At high temperatures, lithium fluoride hydrolyzes to hydrogen fluoride when heated in the presence of moisture. A bifluoride [12159-92-1], $\text{LiF} \cdot \text{HF}$, which forms on reaction of LiF with hydrofluoric acid, is unstable to loss of HF in the solid form.

Lithium fluoride is produced from the reaction of lithium carbonate or hydroxide and hydrofluoric acid. It is a strong flux for glasses, enamels, and glazes and imparts a lower coefficient of expansion to glasses. It is also an important component of fluoride glasses in infrared optical applications. Lithium fluoride is used in brazing or soldering fluxes and in welding (qv) rod coatings. Lithium fluoride, prepared *in situ* from reaction of lithium carbonate and aluminum fluoride, is the active lithium component in improving electrolysis efficiency in aluminum reduction cells.

Lithium Chloride. Lithium chloride [7447-41-8], LiCl, is produced from the reaction of lithium carbonate or hydroxide with hydrochloric acid. The salt melts at 608°C and boils at 1382°C. The 41-mol% LiCl–59-mol% KCl eutectic (melting point, 352°C) is employed as the electrolyte in the molten salt electrolysis production of lithium metal. It is also used, often with other alkali halides, in brazing flux eutectics and other molten salt applications such as electrolytes for high temperature lithium batteries.

The salt is extremely hygroscopic and is used in dehumidification applications. It is very soluble in water (Table 8). The hydrates $\text{LiCl} \cdot 2\text{H}_2\text{O}$ [16712-19-9] and $\text{LiCl} \cdot \text{H}_2\text{O}$ [16712-20-2] precipitate at temperatures below 100°C. The anhydrous salt precipitates at 100°C. The salt has appreciable solubility in alcohols and amines.

Lithium Bromide. Lithium bromide [7550-35-8], LiBr, is prepared from hydrobromic acid and lithium carbonate or lithium hydroxide. The anhydrous salt melts at 550°C and boils at 1310°C. Lithium bromide is a component of the low melting eutectic electrolytes in high temperature lithium batteries.

The salt is extremely soluble in water (Table 4), crystallizing from aqueous solution as the hydrates $\text{LiBr} \cdot \text{H}_2\text{O}$ [23303-71-1], $\text{LiBr} \cdot 2\text{H}_2\text{O}$ [13453-70-8], and $\text{LiBr} \cdot 3\text{H}_2\text{O}$ [76082-04-7]. The anhydrous salt is obtained by drying under vacuum at elevated temperatures.

The high solubility of the salt and resultant low water vapor pressure (69) of its aqueous solutions are useful in absorption air conditioning (qv) systems. Lithium bromide absorption air conditioning technology efficiencies can surpass that of reciprocal technology using fluorochlorocarbon refrigerants.

Basic solutions of lithium bromide can react with oxygen to form hypobromites and bromates under certain conditions.

Lithium Iodide. Lithium iodide [10377-51-2], LiI, is the most difficult lithium halide to prepare and has few applications. Aqueous solutions of the salt can be prepared by careful neutralization of hydroiodic acid with lithium carbonate or lithium hydroxide. Concentration of the aqueous solution leads successively to the trihydrate [7790-22-9], dihydrate [17023-25-5], and monohydrate [17023-24-4], which melt congruently at 75, 79, and 130°C, respectively. The anhydrous salt can be obtained by careful removal of water under vacuum, but because of the strong tendency to oxidize and eliminate iodine which occurs on heating the salt in air, it is often prepared from reactions of lithium metal or lithium hydride with iodine in organic solvents. The salt is extremely soluble in water (62.6 wt% at 25°C) (70) and the solutions have extremely low vapor pressures (71). Lithium iodide is used as an electrolyte in selected lithium battery applications, where it is formed *in situ* from reaction of lithium metal with iodine. It can also be a component of low melting molten salts and as a catalyst in aldol condensations.

12.7. Lithium Hydride. Lithium hydride [7580-67-8], LiH, is prepared by the reaction of lithium metal and hydrogen (qv) in an extremely exothermic reaction. The reaction initiates above the melting temperature of lithium and is then controlled by the hydrogen addition rate to a temperature of about 700°C, slightly above the 686.4°C melting point of lithium hydride (72). Lithium hydride crystallizes in a cubic lattice and has a density of 0.78 g/cm³. It is insoluble in organic solvents but reacts vigorously with protic solvents. The reaction with water produces lithium hydroxide and large volumes of hydrogen, and thus has found applications as a hydrogen source in inflatable devices such as balloons carrying emergency beacons. The lack of solubility of lithium hydride makes it unattractive in most organic reductions. Lithium tetrahydridoaluminate [16853-85-3], LiAlH₄, lithium tetrahydridoborate [16949-15-8], LiBH₄, or other complex hydrides are used instead (61) (see HYDRIDES). The largest industrial use of lithium hydride has been the production of high purity silane from the reaction of silicon halides in a lithium chloride–potassium chloride eutectic (see SILICON COMPOUNDS, SILANES).

12.8. Lithium Hydroxide. Lithium hydroxide monohydrate [1310-66-3], LiOH · H₂O, is prepared industrially from the reaction of lithium carbonate and calcium hydroxide in aqueous slurries. The calcium carbonate is subsequently separated to yield a lithium hydroxide solution from which lithium hydroxide monohydrate can be crystallized. Lithium hydroxide is the least soluble alkali hydroxide, and solubility varies little with temperature.

Lithium hydroxide can be used for preparation of numerous lithium salts. The dominant use is the preparation of lithium stearate [4485-12-5], which is added to lubricating greases in amounts up to about 10% by weight. This salt has very low water solubility and extends the acceptable viscosity for the grease to both low and high temperatures (see LUBRICATION AND LUBRICANTS). Lithium

hydroxide is also used in production of dyes (73) and has been proposed as a source of lithium ion for inhibition of alkali-aggregate expansive reactivity in concrete (74).

Anhydrous lithium hydroxide [1310-65-2], LiOH , is obtained by heating the monohydrate above 100°C . The salt melts at 462°C . Anhydrous lithium hydroxide is an extremely efficient absorbent for carbon dioxide (qv). The porous structure of the salt allows complete conversion to the carbonate with no efficiency loss in the absorption process. Thus LiOH has an important role in the removal of carbon dioxide from enclosed breathing areas such as on submarines or space vehicles. About 750 g of lithium hydroxide is required to absorb the carbon dioxide produced by an individual in a day.

12.9. Lithium Hypochlorite. Lithium hypochlorite [13840-33-0], LiOCl , is obtained from reaction of chlorine and an aqueous solution of lithium hydroxide. The solid is usually obtained as a dry stable product containing other alkali halides and sulfates (75). A product containing 35% available chlorine is used for sanitizing applications in swimming pools and in food preparation areas where its rapid and complete dissolution is important. The salt can also be obtained in higher purity by reaction of lithium hydroxide and hypochlorous acid (76).

12.10. Lithium Niobate. Lithium niobate [12031-64-9], LiNbO_3 , is normally formed by reaction of lithium hydroxide and niobium oxide. The salt has important uses in switches for optical fiber communication systems and is the material of choice in many electrooptic applications including waveguide modulators (77) and sound acoustic wave devices. Crystals of lithium niobate are usually grown by the Czochralski method followed by infiltration of wafers by metal vapor to adjust the index of refraction.

12.11. Lithium Nitrate. Lithium nitrate [7790-69-4] is prepared by neutralization of nitric acid using a lithium base. The nitrate is extremely soluble, 43 wt% at 20°C , in water and is hygroscopic. This salt melts at 251°C and forms very low melting eutectics with a large number of other salts.

12.12. Lithium Nitride. Lithium nitride [26134-62-3], Li_3N , is prepared from the strongly exothermic direct reaction of lithium and nitrogen. The reaction proceeds to completion even when the temperature is kept below the melting point of lithium metal. The lithium ion is extremely mobile in the hexagonal lattice resulting in one of the highest known solid ionic conductivities. Lithium nitride in combination with other compounds is used as a catalyst for the conversion of hexagonal boron nitride to the cubic form. The properties of lithium nitride have been extensively reviewed (78).

12.13. Lithium Oxide. Lithium oxide [12057-24-8], Li_2O , can be prepared by heating very pure lithium hydroxide to about 800°C under vacuum or by thermal decomposition of the peroxide (79). Lithium oxide is very reactive with carbon dioxide or water. It has been considered as a potential high temperature neutron target for tritium production (80).

12.14. Lithium Perchlorate. Lithium perchlorate [7791-03-9], LiClO_4 , is prepared from neutralization of perchloric acid using lithium hydroxide or carbonate. The salt crystallizes from aqueous solution first as the trihydrate. The anhydrous salt, which can be obtained by vacuum drying of the trihydrate at 130°C , melts at 236°C . The salt is kinetically stable up to 400°C (81) decomposing to lithium chloride and oxygen above that temperature. If mixed with catalysts,

decomposition can occur at lower temperatures. Lithium perchlorate has been proposed as a solid rocket fuel oxidant but the most common use is as a lithium battery electrolyte salt. Lithium perchlorate catalyzes Diels-Alder reactions (82), but must be used with precautions (83).

12.15. Lithium Peroxide. Lithium peroxide [12031-80-0], Li_2O_2 , is obtained by reaction of hydrogen peroxide and lithium hydroxide in ethanol (84) or water (85). Lithium peroxide, which is very stable as long as it is not exposed to heat or air, reacts rapidly with atmospheric carbon dioxide releasing oxygen. The peroxide decomposes to the oxide at temperatures above 300°C at atmospheric pressure, and below 300°C under vacuum.

12.16. Lithium Phosphate. Lithium phosphate [10377-52-3], Li_3PO_4 , is prepared from the neutralization of lithium hydroxide using phosphoric acid. Partial neutralization can lead to precipitation of lithium dihydrogen phosphate [13453-80-0], LiH_2PO_4 , but the dilithium monohydrogen phosphate salt cannot be obtained pure from aqueous solution. Lithium phosphate, sparingly soluble (0.039 wt%) in aqueous solution, is used in specialty glasses, including ion-conductive glasses. Lithium phosphate is also a catalyst for the isomerization of epoxides to unsaturated alcohols, most notably the conversion of propylene oxide to allyl alcohol (86).

12.17. Lithium Sulfate. Lithium sulfate [10377-48-7], Li_2SO_4 , is produced from neutralization of sulfuric acid using lithium hydroxide or lithium carbonate. Subsequent evaporation of water from the solution yields first the monohydrate [10102-25-7], $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, and then the anhydrous salt. The dehydration of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ initiates at temperatures as low as 72°C but complete drying can extend over a wide temperature range and is described by a contracting volume model (87). The salt is a component of many photographic developer solutions (see PHOTOGRAPHY).

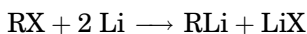
12.18. Lithium Silicate. Lithium silicate [10102-24-6], Li_2SiO_3 , is formed from calcination of lithium carbonate or hydroxide using finely ground silica. The product melts at 1201°C and is insoluble in water. It is used in production of enamels and glazes (see ENAMELS, PORCELAIN OR VITREOUS). Lithium silicate solutions [12627-14-4] containing excess silica can be prepared from the reaction of lithium hydroxide and silica gel. These solutions typically contain a Si:Li mole ratio between four and six and a solids content of around 20%. The solids can be precipitated from solution by adding other salts which, with drying, form insoluble lithium silicate films.

12.19. Other Lithium Salts. A wide range of other lithium salts are emerging in specialized industrial applications. Lithium aluminate [12003-67-7], LiAlO_2 , has important applications in molten carbonate fuel cells and may be useful in fusion reactors. A series of lithium metal oxides are useful in lithium ion batteries, including lithium cobaltite [12190-79-3], LiCoO_2 ; lithium nickelate [12031-65-1], LiNiO_2 ; and various stoichiometries of lithium manganese oxides. Lithium chromate [14307-35-8], Li_2CrO_4 , and lithium molybdate [13568-40-6], Li_2MoO_4 , are both important for corrosion inhibition in lithium halide absorption air conditioning and dehumidification devices. Lithium titanate [12031-82-2], LiTiO_2 , and lithium zirconate [12031-83-3], Li_2ZrO_3 , have important ceramic applications.

13. Organolithium Compounds

Organolithium compounds are organometallic compounds in which the lithium is bonded directly to carbon. Because of the substantial covalent character in these bonds, many of the compounds exist as liquids or as low melting solids and are soluble in organic solvents, such as ethers and liquid hydrocarbons. These compounds are reactive to oxygen and moisture and may ignite spontaneously in the pure state or in concentrated solutions on exposure to air. Organolithium compounds are useful in many Grignard-type reactions employed in the synthesis of pharmaceutical and agricultural products (see GRIGNARD REACTIONS). These compounds are also used as initiators of the stereospecific polymerization of conjugated dienes and vinylaromatic compounds to produce rubbery polymers and plastics.

A simple and economical route involving the reaction of lithium metal and organic halides was developed in 1930 to prepare organolithium compounds such as *n*-butyllithium (88):



This direct method of preparing organolithium compounds is commonly used in commercial processes.

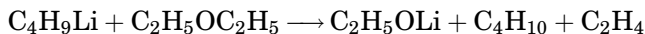
Organolithium compounds generally are less reactive than the other members of the organoalkali series but are more reactive than the Group 2 (IIA) organometallics. However, many differences in type and degree of reaction distinguish organolithiums from other organometallics and make the lithium compounds intermediates in syntheses. Several excellent reviews concerning the preparation, uses, and applications of organolithium compounds are available (89–101), as are yearly reviews (102,103).

13.1. *n*-Butyllithium. The most important organolithium compound is *n*-butyllithium [109-72-8], $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Li}$. *n*-Butyllithium is a clear, colorless-to-pale yellow, slightly viscous liquid that exists in solution in an associated form. Physical properties are given in Table 10.

n-Butyllithium decomposes thermally to 1-butene and lithium hydride at elevated temperatures. Dilute solutions of *n*-butyllithium in hydrocarbon solvents possess a negligible rate of decomposition at ordinary handling temperatures and under an inert atmosphere, eg, argon or nitrogen. For example, the decomposition rate is < 0.01 % active material per day at 25°C for a 15 wt% solution in hexane (108). However, at elevated temperatures and high concentrations of *n*-butyllithium, the losses can be significant. For example, the same 15 wt% solution loses about 0.05% to its active material per day at 45°C, and an 85 wt% solution loses about 0.2 wt%/d at the same temperature. The pyrolysis of alkylolithiums was studied both in neat form (109) and in decane solution (110). A 15 wt% solution of *n*-butyllithium in hexane is 50% decomposed after 5 h at 130°C and after 50 min at 150°C (110). The decomposition rate constants double as the percentage of carbon-bound lithium decreases from 96 to 76% by the addition of lithium *n*-butoxide, the oxidation product of *n*-butyllithium.

Although *n*-butyllithium is quite soluble in ether solvents, its solutions in these solvents are not stable and thus cannot be stored or shipped. A solution

of *n*-butyllithium in diethylether decomposes to give



Ethylene also is a by-product of the cleavage reaction with tetrahydrofuran (111). The rate of loss for *n*-butyllithium in a variety of ether solvents is given in Table 11.

Butyllithium is available in hydrocarbon media, eg, hexane, heptane, cyclohexane, and toluene in several concentrations, eg, 15, 25, and 90 wt%. It is shipped commercially in 10-, 19-, 106-, 216-, and 454-L cylinders and 1900-L (500-gal) tanks and in bulk in 19,000-L (5,000-gal) tank trucks and 30,300-L (8,000-gal) rail tank cars. For shipment purposes, *n*-butyllithium is described as a pyrophoric fuel and is classified as a flammable liquid. As such, full precautions should be taken according to handling instructions (112).

n-Butyllithium solutions are routinely assayed by the following methods.

- (1) The double titration method, which involves the use of benzylchloride, 1,2-dibromoethane, or allyl bromide, determines carbon-bound lithium indirectly (113–115). One sample of the *n*-butyllithium is hydrolyzed directly, and the resulting alkalinity is determined. A second sample is treated with benzylchloride and is then hydrolyzed and titrated with acid. The second value (free base) is subtracted from the first (total base) to give a measure of the actual carbon-bound lithium present (active base).
- (2) The oxidimetric method, which involves the use of solid vanadium pentoxide as oxidant (116). The vanadium is reduced quantitatively by butyllithium and is determined potentiometrically by titration with standard sulfatoceric acid [17106-39-7]. This method gives a direct measure of the actual carbon-bound lithium present when compared to the total titrated alkalinity.
- (3) Other analytical methods which include, among many, a thermometric method (117), a high frequency titration (118), and a colored indicator method (119).

Uses for *n*-butyllithium are mainly as an anionic initiator in solution polymerization to produce elastomeric products and plastics, predominantly of the styrene–butadiene type (120–122) (see ELASTOMERS, SYNTHETIC; INITIATORS, ANIONIC; STYRENE). Butyllithium-initiated polymers of this type can be varied widely in composition and molecular weight in a highly controlled manner, leading to tailor-made products such as footwear, molded and extruded goods, hose and tubing, mechanical rubber goods, adhesives (qv), sealants (qv), and packaging film wrap. A number of reviews are available on organolithium-initiated polymerizations (123–128).

Another large-volume use for organolithium compounds is in the synthesis of pharmaceutical and agricultural chemicals, eg, antibiotics (qv), antihistamines, antidepressants, anticoagulants, vasodilators, tranquilizers, analgesics, fungicides, and pesticides (129–132).

13.2. *sec*-Butyllithium. *sec*-Butyllithium [598-30-1], $\text{CH}_3\text{CH}_2\text{CH}(\text{Li})\text{CH}_3$, is a clear, colorless-to-pale yellow, pyrophoric liquid, $d_{25} = 0.783\text{ g/cm}^3$, viscosity₂₅ = 20.1 mPa · s(= cP) that can be obtained by vacuum distillation of solvent from its hydrocarbon solutions. It can be distilled at about 90°C and 6.7 Pa (0.050 mm Hg) (132). The association state of *sec*-butyllithium is tetrametric (132). *sec*-Butyllithium is available as a 12% solution in *n*-hexane or cyclohexane. These solutions are less stable thermally than those of *n*-butyllithium. Elimination of lithium hydride can occur in a number of ways.

A cis-elimination mechanism has been postulated for this decomposition which follows first-order kinetics (133). The rate is accelerated by addition of lithium *sec*-butoxide [4111-46-0], and other bases, and by an increase in temperature (133). Pyrolysis of *sec*-butyllithium in the presence of added alkoxide is one-half order in alkyl lithium and first order in alkoxide (133). Thermal decomposition of *sec*-butyllithium at 0.18% alkoxide at 25, 40, 50, and 60°C is 0.1%, 0.6%, 2.0%, and 6.8%/d, respectively (134).

Like *n*-butyllithium, *sec*-butyllithium is infinitely soluble in most hydrocarbons, such as pentane and hexane. Its solutions in hexane are flammable and pyrophoric and therefore should be handled like *n*-butyllithium (108,112). *sec*-Butyllithium also is very soluble in ethers, but the ether solutions must be kept cold because ether cleavage is more rapid than in the presence of *n*-butyllithium (135). *sec*-Butyllithium has a $t_{1/2}$ of 2 d at 25°C in di-*n*-butyl ether and of 1 d at 25°C in di-*n*-hexyl ether.

Assay methods for *sec*-butyllithium essentially are identical to those listed for *n*-butyllithium, except that the titrations are performed at lower temperatures because of the lower thermal stability of *sec*-butyllithium.

sec-Butyllithium is available in commercial quantities and is regarded as the second most important organolithium compound. Its uses generally are the same as those for *n*-butyllithium. *sec*-Butyllithium often is the initiator of choice in styrene-butadiene block copolymerizations to produce thermoplastic elastomers. It initiates the polymerization of styrene much faster than *n*-butyllithium, thus permitting the formation of low molecular weight, narrow molecular weight distribution styrene end blocks, with concomitant complete consumption of initiator (136).

13.3. *tert*-Butyllithium. *tert*-Butyllithium [594-19-4], $(\text{CH}_3)_3\text{CLi}$, is a colorless, crystalline solid that can be sublimed at 70–80°C and 13.3 Pa (0.1 mm Hg). Ebullioscopic measurements of the molecular weight in benzene and hexane solution show the average degree of association of *t*-butyllithium to be about four (137).

t-Butyllithium is available as a 15–20 wt% solution in *n*-pentane or heptane. Noticeable decomposition occurs after a 1 h reflux in heptane (bp 98.4°C) but not after a 15 min reflux in benzene (bp 80.1°C) or hexane (bp 68°C). *t*-Butyllithium in pentane or heptane is more stable than *n*-butyllithium in hexane (138). Solutions of *t*-butyllithium in pentane and heptane are flammable liquids and are considered pyrophoric. The *t*-butyl compound is more reactive than either the *n*- and *sec*-butyl. Di-*n*-butyl ether is cleaved by *t*-butyllithium

in 4–5 h at 25°C, compared to the 2 d for *sec*-butyllithium and 32 d for *n*-butyllithium (139). *t*-Butyllithium can be assayed by all of the techniques used for *n*-butyllithium. *t*-Butyllithium is a useful reagent in syntheses where the high reactivity of the carbon–lithium bond and small size of the lithium atom promote the synthesis of sterically hindered compounds, eg, *t*-butyldimethylchlorosilane (130), di-*t*-butyldichlorosilane, and *t*-butyldiphenylchlorosilane.

13.4. Hexyllithium. Hexyllithium [21369-64-2], $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Li}$, is soluble in hexane and other hydrocarbons in high concentrations. Hexyllithium has advantages over butyllithium in metalations where volatility of the by-product hydrocarbon is a factor (140).

13.5. Methyllithium. Methyllithium [917-54-4], CH_3Li , crystallizes from benzene or hexane solution giving cubic crystals that have a salt-like constitution (141). Crystalline methyllithium molecules exist as tetrahedral tetramers (142). Solutions of methyllithium are less reactive than those of its higher homologues. Methyllithium is stable for at least six months in diethyl ether at room temperature. A one-molar solution of methyllithium in tetrahydrofuran (14 wt%) and cumene (83 wt%) containing 0.08 *M* dimethylmagnesium as stabilizer loses only 0.008% of its activity per day at 15°C and is nonpyrophoric (130).

Methyllithium solutions can be assayed by the methods used for *n*-butyllithium, by gas chromatography (qv), or by nmr. Reaction with dimethyl-(phenyl)chlorosilane gives the silane $(\text{CH}_3)_3\text{SiC}_6\text{H}_5$, which is determined quantitatively using a silicone fluid 710 X Chromosorb P column with cumene as an internal standard (143). Methyllithium is available in commercial quantities. It is a useful reagent in the synthesis of vitamins A and D and in the synthesis of various analgesics and steroids (qv) (see ANALGESICS, ANTIPYRETICS, AND ANTIINFLAMMATORY AGENTS; VITAMINS).

13.6. Lithium Acetylide. Lithium acetylide–ethylenediamine complex [50475-76-8], $\text{LiC}\equiv\text{CH}\cdot\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$, is obtained as colorless-to-light-tan, free-flowing crystals from the reaction of *N*-lithioethylenediamine and acetylene in an appropriate solvent (144). The complex decomposes slowly above 40°C to lithium carbide and ethylenediamine. Lithium acetylide–ethylenediamine is very soluble in primary amines, ethylenediamine, and dimethyl sulfoxide. It is slightly soluble in ether, THF, and secondary and tertiary amines, and is insoluble in hydrocarbons.

Stabilized lithium acetylide is not pyrophoric or shock-sensitive as are the transition-metal acetylides. Among its uses are ethynylation of halogenated hydrocarbons to give long-chain acetylenes (145) and ethynylation of ketosteroids and other ketones in the pharmaceutical field to yield the respective ethynyl alcohols (146) (see ACETYLENE-DERIVED CHEMICALS).

Lithium acetylide also can be prepared directly in liquid ammonia from lithium metal or lithium amide and acetylene (147). In this form, the compound has been used in the preparation of β -carotene and vitamin A (148), ethchlorvynol (149), and *cis*-3-hexen-1-ol (leaf alcohol) (150). More recent synthetic processes involve preparing the lithium acetylide *in situ*. Thus lithium diisopropylamide, prepared from *n*-butyllithium and the amine in THF at 0°C, is added to an acetylene-saturated solution of a ketosteroid to directly produce an ethynylated steroid (151).

13.7. Phenyllithium. Phenyllithium [591-51-5], C_6H_5Li , forms colorless, monoclinic, pyrophoric crystals that do not melt before decomposition at $150^\circ C$. It can be obtained from its halide-free solutions in cyclohexane and ethylether by vacuum distillation to remove the ether. The usual preparative method is by reaction of chloro- or bromobenzene and lithium metal in ethyl ether or in a mixture of ethyl ether and cyclohexane.

Phenyllithium can be used as a solution in ethyl ether, but because of its limited stability ($t_{1/2} = 12$ d at $35^\circ C$) it is commercially available in solution in mixtures, usually 70:30 wt% cyclohexane:ethyl ether (130). In this particular mixture of solvents, a 20 wt% solution, free of chlorobenzene, is stable for at least four months under an inert atmosphere (argon or nitrogen) in sealed containers at room temperature. Phenyllithium is also available in dibutyl ether solution (130). It is classified as a flammable liquid.

Phenyllithium can be used in Grignard-type reactions involving attachment of phenyl group, eg, in the preparation of analgesics and other chemotherapeutic agents (qv). It also may be used in metal-metal interconversion reactions leading, eg, to phenyl-substituted silicon and tin organics.

13.8. Other Organolithium Compounds. Organodilithium compounds have utility in anionic polymerization of butadiene and styrene. The lithium chain ends can then be converted to useful functional groups, eg, carboxyl, hydroxyl, etc (152). Lewis bases are required for solubility in hydrocarbon solvents.

Many organic syntheses require the use of sterically hindered and less nucleophilic bases than *n*-butyllithium. Lithium diisopropylamide (LDA) and lithium hexamethyldisilazide (LHS) are often used (153–155). Both compounds are soluble in a wide variety of aprotic solvents. Presence of a Lewis base, most commonly tetrahydrofuran, is required for LDA solubility in hydrocarbons. A 30% solution of LHS can be prepared in hexane. Although these compounds may be prepared by reaction of the amine with *n*-butyllithium in the appropriate medium just prior to use, they are also available commercially in hydrocarbon or mixed hydrocarbon-THF solvents as 1.0–2.0 *M* solutions.

Other, even milder bases than LDA and LHS, such as lithium methoxide and lithium *t*-butoxide, may be used in organic syntheses (156,157). Lithium methoxide is available commercially as a 10% solution in methanol and lithium *t*-butoxide as an 18% solution in tetrahydrofuran (158). Lithium *t*-butoxide is also soluble in hydrocarbon solvents (159). Both lithium alkoxides are also available as solids (160) (see ALKOXIDES, METAL).

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Table 1. Salar Ion Concentrations

Country	Salar or lake	Ion composition, wt%				Reference
		Li	Mg	K	Na	
Chile	Salar de Atacama	0.15	0.96	1.80	7.6	8
Bolivia	Salar de Uyuni	0.096	2.0	1.67	9.1	9
Argentina	Salar del Hombre Muerto	0.062	0.089	0.61	10.4	10
United States	Great Salt Lake, Utah	0.006	0.8	0.4	7.0	7
	Salton Sea, Calif.	0.022	0.028	1.42	5.71	7
	Searles Lake, Calif.	0.0083	0.034	2.30	15.20	7
	Silver Peak, Nev.	0.03	0.04	0.8	6.20	7
Israel–Jordan	Dead Sea	0.002	3.40	0.6	3.00	7
People's Republic of China	Lake Zabuye	0.097	0.001	2.64	10.80	11

Table 2. World Mine Production, Reserves, and Reserve Base of Lithium, t^a

	Mine production		Reserves ^b	Reserve base ^b
	2002	2003 ^c		
United States	W ^d	W ^d	38,000	410,000
Argentina ^c	946	940	NA	NA
Australia ^c	3,140	3,200	160,000	260,000
Bolivia				5,400,000
Brazil	224	240	190,000	910,000
Canada	707	700	180,000	360,000
Chile	5,920	5,900	3,000,000	3,000,000
China	2,400	2,400	540,000	1,100,000
Portugal	190	200	NA	NA
Zimbabwe	640	640	23,000	27,000
<i>World total (rounded)</i>	<i>14,200^e</i>	<i>14,200^e</i>	<i>4,100,000</i>	<i>11,000,000</i>

^aRef. 15.^bNA = not available.^cEstimated.^dWithheld to disclose proprietary data.^eExcludes U.S. production.

Table 3. **Physical Properties of Lithium**

Property	Value	Reference
at. vol, cm ³	13.0	
mp, °C	180.5	35
bp, °C	1336	36
first ionization potential, kJ/mol ^a	519	37
electron affinity, kJ/mol ^a	52.3	37
crystal structure	bcc	
lattice constant, pm	350	37
radius, pm		
metallic	122.5	37
ionic	60	
<i>d</i> ₂₀ , g/cm ³	0.531	38
specific heat, J/g ^a		
at 25 °C	3.55	35
liquid at mp	4.39	35
heat of fusion, J/g ^a	431.8	35
heat of vaporization, kJ/g ^a	ca 21.3	39
electrical resistivity at 20°C, μΩ · cm	9.446	40
characteristic spectrum lines, nm		
red	670.8	
orange	610.4	
vapor pressure, kPa ^b		35
at 702°C	0.065	
802°C	0.376	
902°C	1.61	
1002°C	5.47	
1052°C	9.4	
1077°C	12.13	

^aTo convert J to cal, divide by 4.184.

^bMore extensive vapor pressure data for lithium and other metals are given in Ref. 41. To convert kPa to mm Hg, multiply by 7.5.

Table 4. U.S. Salient Statistics for Lithium^{a,b}

Sector	1999	2000	2001	2002	2003 ^c
production, t	W	W	W	W	W
imports for consumption, t	2,640	2,880	1,990	1,920	2,200
exports, t	1,330	1,310	1,480	1,620	1,700
consumption					
apparent	W	W	W	W	W
estimated	2,800	2,800	1,400	1,100	1,300
price, year end, \$/kg					
lithium carbonate	4.47	4.47	NA	NA	NA
lithium hydroxide, monohydrate	5.74	5.74	NA	NA	NA
employment, mine and mill, number ^c	100	100	100	100	100
net import reliance ^d as a percentage of apparent consumption	<50%	<50%	<50%	<50%	<50%

^aRef. 15.^bW = withheld, NA = not available.^cEstimated.^dImports – exports + adjustments for stock changes.

Table 5. U.S. Imports for consumption of Lithium Chemicals
by Country^{a,b}

Compound and country	2001		2002	
	Gross Weight, t	Value ^c × 10 ³ \$	Gross weight, t	Value ^c × 10 ³ \$
<i>Lithium carbonate</i>				
Argentina	808	1,290	882	2,010
Chile	9,160	13,200	8,660	12,800
France	0	0	11	32
Germany	10	28	15	49
Japan	1	6	138	268
Mexico	113	87	36	27
New Zealand	145	577	31	121
other	22 ^d	78 ^d	59	210
<i>Total</i>	10,300	15,300	9,830	15,600
<i>Lithium hydroxide</i>				
China	341	901	401	1,060
Japan	5	66	14	145
United Kingdom	15	246	6	38
other	1	23	11	44
<i>Total</i>	362	1,240	432	1,290

^aRef. 49

^bData are rounded to no more than three significant digits; may not add to totals shown.

^cCustoms value.

^dRevised.

Table 6. U.S. Exports of Lithium Chemicals, By Country^a

Compound and country	2001		2002	
	Gross weight, t	Value, $\times 10^3$ \$	Gross weight, t	Value, $\times 10^3$ \$
<i>Lithium carbonate</i>				
Australia	0	0	130	551
Canada	410	1,470	331	1,190
China	29	108	100	361
Germany	865	2,360	1,100	3,120
India	22	78	53	162
Japan	1,080	4,020	1,450	4,800
Korea, Republic of	26	92	25	90
Mexico	3	14	7	25
Netherlands	88	317	90	333
Taiwan	9	33	20	71
United Kingdom	247	763	175	582
other	136	556	138	626
<i>Total</i>	<i>2,920</i>	<i>9,810</i>	<i>3,620</i>	<i>11,900</i>
<i>Lithium carbonate U.S.P.^b</i>				
Australia	50	226	45	182
China	20	35	39	71
Germany	64	117	138	276
Israel	2	67	1	26
Singapore	19	39	0	0
Sweden	13	57	0	0
Venezuela	100	170	0	0
other	13 ^c	119 ^c	28	122
<i>Total</i>	<i>281</i>	<i>830</i>	<i>251</i>	<i>677</i>
<i>Lithium hydroxide</i>				
Argentina	96	324	69	208
Australia	189	788	56	237
Canada	326	1,290	132	515
Chile	39	142	24	107
China	15	36	22	88
Germany	516	1,540	646	2,000
India	298	858	521	1,320
Japan	910	4,780	759	3,700
Korea, Republic of	237	909	241	846
Mexico	98	344	55	191
Netherlands	172	431	103	406
New Zealand	266	1,100	22	80
Philippines	32	100	17	49
Singapore	86	359	108	395
Thailand	109	286	87	233
Taiwan	36	163	23	92
United Kingdom	245	1,490	194	1,170
other	1,630	7,510	2,320	9,000
<i>Total</i>	<i>5,300</i>	<i>22,400</i>	<i>5,400</i>	<i>20,600</i>

^aRef. 49.^bRevised Pharmaceutical-grade lithium carbonate.

Table 7. **Properties of Lithium Fluoride**

Property	Value	Reference
melting point, °C	848	59
boiling point, °C	1681	59
solubility, g/100 g solvent		
water, 25.4°C	0.133	60
water, 81.8°C	0.150	60
acetic acid, 25°C	0.084	61
acetic acid, 50°C	0.152	61
liquid HF, 12°C	10.3	62
tetrahydrofuran, 25°C	0.6	63
crystalline form	cubic (NaCl)	64
a_0 , nm	0.401736	
density at 20°C, g/cm ³	2.635	64
index of refraction	1.3915	64
lattice energy, kJ/mol ^a	1020 ± 10	65
standard heat of formation, kJ/mol ^a	−613.0	59
standard entropy, J/(mol·K) ^a	35.9	59
heat capacity, C_p , J/(mol·K) ^a	42.01	59
heat of fusion, kJ/mol ^b	27.09	59
heat of vaporization, kJ/mol ^b	213	66
heat of hydration, kJ/mol ^b	1.023	66
debye temperature	449	67

^aTo convert kJ to kcal, divide by 4.184.

Table 8. **Lithium Chloride and Lithium Bromide Solubility in Water^a**

Temperature, °C	Lithium salt, wt %	Solid-phase formula
<i>LiCl</i>		
0	40.2	$\text{LiCl} \cdot 2\text{H}_2\text{O}$
19.4	45.2	$\text{LiCl} \cdot 2\text{H}_2\text{O} + \text{LiCl} \cdot \text{H}_2\text{O}$
20	45.2	$\text{LiCl} \cdot \text{H}_2\text{O}$
50	48.3	$\text{LiCl} \cdot \text{H}_2\text{O}$
80	53.0	$\text{LiCl} \cdot \text{H}_2\text{O}$
95	56.0	$\text{LiCl} \cdot \text{H}_2\text{O} + \text{LiCl}$
100	56.3	LiCl
<i>LiBr</i>		
0	56.7	$\text{LiBr} \cdot 3\text{H}_2\text{O}$
3	58.3	$\text{LiBr} \cdot 3\text{H}_2\text{O} + \text{LiBr} \cdot 2\text{H}_2\text{O}$
20	60.2	$\text{LiBr} \cdot 2\text{H}_2\text{O}$
30	62.0	$\text{LiBr} \cdot 2\text{H}_2\text{O}$
42.7	65.0	$\text{LiBr} \cdot 2\text{H}_2\text{O} + \text{LiBr} \cdot \text{H}_2\text{O}$
50	65.5	$\text{LiBr} \cdot \text{H}_2\text{O}$
80	67.8	$\text{LiBr} \cdot \text{H}_2\text{O}$
100	69.5	$\text{LiBr} \cdot \text{H}_2\text{O}$

^aRef. 68.

Table 9. **Solubility of Lithium Monohydrate in Water**

Temperature, °C	Solubility in water, wt %
0	18.8
10	18.9
20	19.1
40	19.8
60	21.0
80	23.0
100	25.9

Table 10. **Physical Constants of *n*-Butyllithium**

Property	Value	Reference
distillation range at 13.3 mPa, ^a °C	80–90	104
d_{25} , g/cm ³	0.765	105
viscosity, mPa · s(=cP)		
at 25°C	34.6	
0.1°C	119.6	105
heat of formation at 25°C, kJ/mol ^b	–133.9 + 7.1	106
	–131.4 ± 2.9	107
vapor pressure, mPa ^a		
at 60°C	58.3	108
80°C	592	108
95°C	2590	108

^aTo convert mPa to mm Hg, multiply by 7.5×10^{-6} .^bTo convert J to cal, divide by 4.184.

Table 11. **Decomposition of *n*-Butyllithium in Ethers**

Ether	$t_{1/2}^a$	Temperature, °C
ethyl	6	25
	31 ^b	35
isopropyl	18	25
glycol dimethyl	10 ^c	25
tetrahydrofuran	23.5 ^b	0
	5	−30

^aUnits are days unless otherwise noted.^bUnits are hours.^cUnits are minutes.