# Lithium

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**Lithium** (from Greek:  $\lambda(\theta \circ \zeta \ lithos$ , "stone") is a chemical element with the symbol **Li** and atomic number 3. It is a soft, silver-white metal belonging to the alkali metal group of chemical elements. Under standard conditions, it is the lightest metal and the least dense solid element. Like all alkali metals, lithium is highly reactive and flammable. For this reason, it is typically stored in mineral oil. When cut open, it exhibits a metallic luster, but contact with moist air corrodes the surface quickly to a dull silvery gray, then black tarnish. Because of its high reactivity, lithium never occurs freely in nature, and instead, appears only in compounds, which are usually ionic. Lithium occurs in a number of pegmatitic minerals, but due to its solubility as an ion, is present in ocean water and is commonly obtained from brines and clays. On a commercial scale, lithium is isolated electrolytically from a mixture of lithium chloride and potassium chloride.

The nucleus of the lithium atom verges on instability, since the two stable lithium isotopes found in nature have among the lowest binding energies per nucleon of all stable nuclides. Because of its relative nuclear instability, lithium is less common in the solar system than 25 of the first 32 chemical elements even though the nuclei are very light in atomic weight. For related reasons, lithium has important links to nuclear physics. The transmutation of lithium atoms to helium in 1932 was the first fully man-made nuclear reaction, and lithium-6 deuteride serves as a fusion fuel in staged thermonuclear weapons. [4]

Lithium and its compounds have several industrial applications, including heatresistant glass and ceramics, lithium grease lubricants, flux additives for iron, steel and aluminium production, lithium batteries, and lithium-ion batteries. These uses consume more than three quarters of lithium production.

Trace amounts of lithium are present in all organisms. The element serves no apparent vital biological function, since animals and plants survive in good health without it, though non-vital functions have not been ruled out. The lithium ion Li<sup>+</sup> administered as any of several lithium salts has proved to be useful as a mood-stabilizing drug in the treatment of bipolar disorder in humans.

## Lithium, 3Li



Lithium floating in oil



Spectral lines of lithium

#### **General properties**

Name, symbol lithium, Li

**Pronunciation** /'lɪθiəm/

**∟ı-**thee-əm

**Appearance** silvery-white

#### Lithium in the periodic table

Atomic number (Z) 3

**Group, block** group 1 (alkali metals),

s-block

**Period** period 2

**Element category**  $\square$  alkali metal

**Standard atomic** 

6.997)[2]

6.94<sup>[1]</sup> (6.938-

weight  $(A_r)$ 

[He] 2s<sup>1</sup>

Electron configuration

per shell 2, 1

## **Properties**

## **Atomic and physical**



Lithium ingots with a thin layer of black nitride tarnish

Like the other alkali metals, lithium has a single valence electron that is easily given up to form a cation.<sup>[5]</sup> Because of this, lithium is a good conductor of heat and electricity as well as a highly reactive element, though it is the least reactive of the alkali metals. Lithium's low reactivity is due to the proximity of its valence electron to its nucleus (the remaining two electrons are in the 1s orbital, much lower in energy, and do not participate in chemical bonds).<sup>[5]</sup>

Lithium metal is soft enough to be cut with a knife. When cut, it possesses a silvery-white color that quickly changes to gray as

it oxidizes to lithium oxide.<sup>[5]</sup> While it has one of the lowest melting points among all metals (180 °C), it has the highest melting and boiling points of the alkali metals.<sup>[6]</sup>

Lithium has a very low density (0.534 g/cm³), comparable with pine wood. It is the least dense of all elements that are solids at room temperature; the next lightest solid element (potassium, at 0.862 g/cm³) is more than 60% denser. Furthermore, apart from helium and hydrogen, it is less dense than any liquid element, being only two thirds as dense as liquid nitrogen (0.808 g/cm³).<sup>[7]</sup> Lithium can float on the lightest hydrocarbon oils and is one of only three metals that can float on water, the other two being sodium and potassium.

Lithium's coefficient of thermal expansion is twice that of aluminium and almost four times that of iron. Lithium is superconductive below 400  $\mu$ K at standard pressure and at higher temperatures (more than 9 K) at very high pressures (>20 GPa). At temperatures below 70 K, lithium, like sodium, undergoes diffusionless phase change transformations. At 4.2 K it has a rhombohedral crystal system (with a nine-layer repeat spacing); at higher temperatures it transforms to face-centered cubic and then

Physical properties				
Phase	solid			
Melting point	453.65 K (180.50 °C, 356.90 °F)			
Boiling point	1603 K (1330 °C, 2426 °F)			
<b>Density</b> near r.t.	0.534 g/cm <sup>3</sup>			
when liquid, at m.p.	0.512 g/cm <sup>3</sup>			
Critical point	3220 K, 67 MPa (extrapolated)			
<b>Heat of fusion</b>	3.00 kJ/mol			
Heat of vaporization	136 kJ/mol			

Molar heat capacity

#### Vapor pressure

24.860 I/(mol·K)

<b>P</b> (Pa)	1	10	100	1 k	10 k	100 k
at T (K)	797	885	995	1144	1337	1610

#### **Atomic properties**

Oxidation states	+1 (a strongly basic
	oxide)

**Electronegativity** Pauling scale: 0.98 **Ionization** 1st: 520.2 kJ/mol energies 2nd: 7298.1 kJ/mol

gies 2nd: 7298.1 kJ/mol 3rd: 11815.0 kJ/mol

**Atomic radius** empirical: 152 pm

**Covalent radius** 128±7 pm

Van der Waals radius 182 pm

#### Miscellanea

**Crystal structure** body-centered cubic

(bcc)



Lithium floating in oil

body-centered cubic. At liquid-helium temperatures (4 K) the rhombohedral structure is prevalent.<sup>[11]</sup> Multiple allotropic forms have been identified for lithium at high pressures.<sup>[12]</sup>

Lithium has a mass specific heat capacity of 3.58 kilojoules per kilogram-kelvin, the highest of all solids.<sup>[13][14]</sup> Because of this, lithium metal is often used in coolants for heat transfer applications.<sup>[13]</sup>

## **Chemistry and compounds**

Lithium reacts with water easily, but with noticeably less energy than other alkali metals. The reaction forms hydrogen gas and lithium hydroxide in aqueous solution.<sup>[5]</sup> Because of its reactivity with water, lithium is usually stored in a hydrocarbon

sealant, often petroleum jelly. Though the heavier alkali metals can be stored in more dense substances, such as mineral oil, lithium is not dense enough to be fully submerged in these liquids. <sup>[15]</sup> In moist air, lithium rapidly tarnishes to form a black coating of lithium hydroxide (LiOH and LiOH·H<sub>2</sub>O), lithium nitride (Li<sub>3</sub>N) and lithium carbonate (Li<sub>2</sub>CO<sub>3</sub>, the result of a secondary reaction between LiOH and CO<sub>2</sub>). <sup>[16]</sup>

When placed over a flame, lithium compounds give off a striking crimson color, but when it burns strongly the flame becomes a brilliant silver. Lithium will ignite and burn in oxygen when exposed to water or water vapors. [17] Lithium is flammable, and it is potentially explosive when exposed to air and especially to water, though less so than the other alkali metals. The lithium-water reaction at normal temperatures is brisk but nonviolent because the hydrogen produced does not ignite on its own. As with all alkali metals, lithium fires are difficult to extinguish, requiring dry powder fire extinguishers (Class D type). Lithium is the only metal which reacts with nitrogen under normal conditions. [18][19]

Lithium has a diagonal relationship with magnesium, an element of similar atomic and ionic radius. Chemical resemblances between the two metals include the formation of a nitride by reaction with  $N_2$ , the formation of an oxide ( $Li_2O$ ) and



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Speed of sound thin rod	6000 m/s (at 20 °C)		
Thermal expansion	46 μm/(m·K) (at 25 °C		
Thermal conductivity	84.8 W/(m·K)		
Electrical resistivity	92.8 nΩ·m (at 20 °C)		
Magnetic ordering	paramagnetic		
Young's modulus	4.9 GPa		
Shear modulus	4.2 GPa		
Bulk modulus	11 GPa		
Mohs hardness	0.6 5 MPa		
Brinell hardness			
CAS Number	7439-93-2		
His	story		
Discovery	Johan August Arfwedson (1817)		
First isolation	William Thomas Brande (1821)		

#### Most stable isotopes of lithium

iso	NA	half-life	DM	<b>DE</b> (MeV)	DP
<sup>6</sup> Li	5%	is stable with 3 neutrons			
<sup>7</sup> Li	95%	is stab	le witl	n 4 neutrons	

<sup>6</sup>Li content may be as low as 3.75% in natural samples. <sup>7</sup>Li would therefore have a content of up to 96.25%.



Hexameric structure of the nbutyllithium fragment in a crystal

peroxide ( $\text{Li}_2\text{O}_2$ ) when burnt in  $\text{O}_2$ , salts with similar solubilities, and thermal instability of the carbonates and nitrides.<sup>[16][20]</sup> The metal reacts with hydrogen gas at high temperatures to produce lithium hydride (LiH).<sup>[21]</sup>

Other known binary compounds include halides (LiF, LiCl, LiBr, Lil), sulfide (Li $_2$ S), superoxide (LiO $_2$ ), and carbide (Li $_2$ C $_2$ ). Many other inorganic compounds are known in which lithium combines with anions to form salts: borates, amides, carbonate, nitrate, or borohydride (LiBH $_4$ ). Lithium aluminium hydride (LiAlH $_4$ ) is commonly used as a reducing agent in organic synthesis.

Multiple organolithium reagents are known in which there is a direct bond between carbon and lithium atoms, effectively creating a carbanion. These are extremely powerful bases and nucleophiles. In many of these organolithium compounds, the lithium ions tend to aggregate into high-symmetry clusters by themselves, which is relatively common for alkali cations.<sup>[22]</sup> LiHe, a very weakly interacting van der Waals compound, has been detected at very low temperatures.<sup>[23]</sup>

## **Isotopes**

Naturally occurring lithium is composed of two stable isotopes,  $^6\text{Li}$  and  $^7\text{Li}$ , the latter being the more abundant (92.5% natural abundance). Both natural isotopes have anomalously low nuclear binding energy per nucleon (compared to the neighboring elements on the periodic table, helium and beryllium); lithium is the only low numbered element that can produce net energy through nuclear fission. The two lithium nuclei have lower binding energies per nucleon than any other stable nuclides other than deuterium and helium-3. As a result of this, though very light in atomic weight, lithium is less common in the Solar System than 25 of the first 32 chemical elements. Seven radioisotopes have been characterized, the most stable being Li with a half-life of 838 ms and Li with a half-life of 178 ms. All of the remaining radioactive isotopes have half-lives that are shorter than 8.6 ms. The shortest-lived isotope of lithium is  $^4\text{Li}$ , which decays through proton emission and has a half-life of 7.6 ×  $^{10^{-23}}$  s. [26]

<sup>7</sup>Li is one of the primordial elements (or, more properly, primordial nuclides) produced in Big Bang nucleosynthesis. A small amount of both <sup>6</sup>Li and <sup>7</sup>Li are produced in stars, but are thought to be "burned" as fast as produced.<sup>[27]</sup> Additional small amounts of lithium of both <sup>6</sup>Li and <sup>7</sup>Li may be generated from solar wind, cosmic rays hitting heavier atoms, and from early solar system <sup>7</sup>Be and <sup>10</sup>Be radioactive decay.<sup>[28]</sup> While lithium is created in stars during stellar nucleosynthesis, it is further burned. <sup>7</sup>Li can also be generated in carbon stars.<sup>[29]</sup>

Lithium isotopes fractionate substantially during a wide variety of natural processes,  $^{[30]}$  including mineral formation (chemical precipitation), metabolism, and ion exchange. Lithium ions substitute for magnesium and iron in octahedral sites in clay minerals, where  $^6$ Li is preferred to  $^7$ Li, resulting in enrichment of the light isotope in processes of hyperfiltration and rock alteration. The exotic  $^{11}$ Li is known to exhibit a nuclear halo. The process known as laser isotope separation can be used to separate lithium isotopes, in particular  $^7$ Li from  $^6$ Li.  $^{[31]}$ 

Nuclear weapons manufacture and other nuclear physics applications are a major source of artificial lithium fractionation, with the light isotope <sup>6</sup>Li being retained by industry and military stockpiles to such an extent that it has caused slight but measurable change in the <sup>6</sup>Li to <sup>7</sup>Li ratios in natural sources, such as rivers. This has led to unusual uncertainty in the standardized atomic weight of lithium, since this quantity depends on the natural abundance ratios of these naturally-occurring stable lithium isotopes, as they are available in commercial lithium mineral sources.<sup>[32]</sup>

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