

## LEAD CARBONATE, BASIC

[1319-46-6]

Formula:  $\text{Pb}(\text{OH})_2 \cdot 2\text{PbCO}_3$ ; MW 775.60; phase rule study indicates the existence of basic lead carbonates of other compositions:  $3\text{PbO} \cdot 5\text{PbCO}_3$ ;  $\text{PbO} \cdot \text{PbCO}_3$ ;  $2\text{PbO} \cdot \text{PbCO}_3$

Synonyms: white lead; basic carbonate

### Uses

White lead, in the basic carbonate form, was used extensively as white pigment in paint until its toxic properties became known. At present, most of its pigment applications are as red-reflecting pigment in plastic sheets; in UV light-reflecting paints; in ceramic glaze; and in many temperature-sensitive inks that cause color change. Other applications include use as a catalyst in terephthalic acid reactions with diols; as a heat-sensitive stabilizer for poly vinyl chloride polymers; in lubricating grease, and as a curing agent to improve polyethylene wire insulation.

### Preparation

Many commercial processes have been developed for manufacturing basic lead carbonate. These include: Thomson-Stewart process, Carter process, and Dutch process. The method of preparation involves treating lead with acetic acid vapors in the presence of carbon dioxide at 60°C. In the Thomson-Stewart process, finely divided lead monoxide or lead metal is mixed with water to give aqueous slurry, which is then mixed with acetic acid in the presence of air and carbon dioxide. All these processes are slow, taking weeks to obtain products of desired composition.

Basic lead carbonate also is precipitated by dissolving lead monoxide in lead(II) acetate solution, and treating the solution with carbon dioxide. It also is produced by electrolysis of sodium nitrate or sodium acetate using lead anode and then precipitating out the product by adding sodium carbonate.

### Analysis

The basic carbonates have varying compositions. They may be characterized by elemental analysis, x-ray methods and also by their physical properties.

## LEAD CHROMATE

[7758-97-6]

Formula:  $\text{PbCrO}_4$ ; MW 323.19

Synonyms: chrome yellow; crocoite

### Occurrence and Uses

Lead chromate occurs in nature as the minerals, crocoite and phoenic-chroite. It is an important pigment of lead used in oil paints and water col-

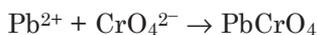
ors. It is used for printing textiles and coloring porcelain.

### Physical Properties

Yellow monoclinic crystals; refractive index 2.31; density 6.12 g/cm<sup>3</sup>; melts at 844°C; decomposes on further heating; insoluble in water; also insoluble in ammonia and acetic acid; soluble in acids and alkalies.

### Production

Lead chromate is found naturally in minerals crocoite and phoenicochroite. It also is readily prepared by adding a soluble chromate such as sodium or potassium chromate to a solution of lead nitrate, lead acetate or other soluble lead(II) salt in neutral or slightly acidic solution:



The yellow precipitate is filtered, washed and dried.

### Analysis

Elemental composition: Pb 64.11%, Cr 16.09%, O 19.80%. Lead chromate may be identified from its physical properties and x-ray crystallography. Lead and chromium can be measured in a nitric acid solution of the compound by AA, ICP, and other instrumental methods. (See Lead.)

### Toxicity

Moderately toxic by intraperitoneal route. The effects, however, are mild from oral intake. Occupational exposure may cause cancer. There is sufficient evidence of carcinogenicity in animals and humans.

## LEAD DICHLORIDE

[7758-95-4]

Formula: PbCl<sub>2</sub>; MW 278.11

Synonyms: lead(II) chloride; lead chloride

### Occurrence and Uses

Lead dichloride occurs in nature as the mineral cotunnite. The compound is used in making many basic chlorides, such as Pattison's lead white, Turner's Patent Yellow, and Verona Yellow, used as pigments. Also, it is used as a flux for galvanizing steel; as a flame retardant in nylon wire coatings; as a cathode for seawater batteries; to remove H<sub>2</sub>S and ozone from effluent gases; as a sterilization indicator; as a polymerization catalyst for alpha-olefins; and as a co-catalyst in manufacturing acrylonitrile.

### Physical Properties

White orthorhombic crystals; refractive index 2.199; density 5.85 g/cm<sup>3</sup>; melts at 501°C; vaporizes at 950°C; partially soluble in cold water (6.73 g/L at

0°C and 9.9 g/L at 20°C);  $K_{SP}$   $1.17 \times 10^{-5}$  at 25°C; moderately soluble in boiling water (33.4 g/L at 100°C); slightly soluble in dilute HCl and ammonia; insoluble in alcohol.

### Thermochemical Properties

$\Delta H_f^\circ$	-85.90 kcal/mol
$\Delta G_f^\circ$	-75.98 kcal/mol
$S^\circ$	32.50 cal/degree mol

### Preparation

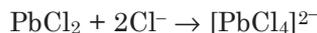
Lead dichloride is precipitated by adding hydrochloric acid or any chloride salt solution to a cold solution of lead nitrate or other lead(II) salt:



Alternatively, it is prepared by treating lead monoxide or basic lead carbonate with hydrochloric acid and allowing the precipitate to settle.

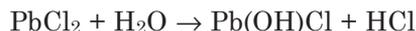
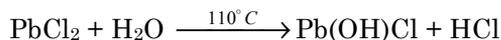
### Reactions

In dilute solutions of hydrochloric acid or halide ion, solubility of lead dichloride decreases; however, in concentrated solutions, solubility increases due to formation of the complex ion, tetrachloroplumbate(II),  $[\text{PbCl}_4]^{2-}$ :



The latter also forms complex salts of alkali metals  $\text{M}_2\text{PbCl}_4$  and  $\text{MPb}_2\text{Cl}_5$ .

Lead dichloride is hydrolyzed by steam to a basic chloride  $\text{Pb}(\text{OH})\text{Cl}$  and hydrochloric acid:



Aqueous solution of lead dichloride also undergoes double decomposition reactions with several metal salts, precipitating insoluble lead salts.

When an aqueous solution of lead dichloride is mixed with caustic soda or other alkalis, basic chlorides such as  $\text{PbCl}_2 \cdot \text{Pb}(\text{OH})_2$  are formed. They are used as pigments.

### Analysis

Elemental composition: Pb 74.50%, Cl 25.49%. Lead chloride may be identified by its physical properties and using x-ray analysis. An aqueous solution may be analyzed for lead by AA, ICP and other instrumental techniques, and for chloride ion by ion chromatography, or by titration with a standard solution of silver nitrate or mercuric nitrate.

**Toxicity**

Toxic effects from ingestion may vary from low to moderate. The oral lethal dose in guinea pigs is documented as 1,500 mg/kg. (Lewis (Sr.), R. J. 1996. *Sax's Dangerous Properties of Industrial Materials*, 9<sup>th</sup> ed. New York: Van Nostrand Reinhold).

**LEAD DIFLUORIDE**

[7783-46-2]

Formula: PbF<sub>2</sub>; MW 245.20

Synonyms: lead fluoride; lead(II) fluoride; plumbous fluoride

**Uses**

Lead difluoride is used in low melting glasses; in glass coatings to reflect infrared rays; in phosphors for television-tube screens; for nickel plating on glass; and as a catalyst for the manufacture of picoline.

**Physical Properties**

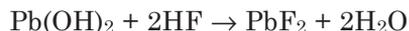
Colorless orthorhombic crystals or white powder; converts to cubic form at 316°C; density 8.445 g/cm<sup>3</sup> (orthorhombic form) and 7.750 g/cm<sup>3</sup> (cubic form); melts at 855°C; vaporizes at 1,290°C; slightly soluble in water (640 mg/L at 20°C); K<sub>SP</sub> 7.12x10<sup>-7</sup> at 25°C; soluble in nitric acid; insoluble in acetone and ammonia.

**Thermochemical Properties**

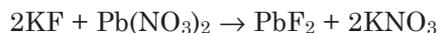
$\Delta H_f^\circ$	-158.7 kcal/mol
$\Delta G_f^\circ$	-147.5 kcal/mol
S°	26.4 cal/degree mol

**Preparation**

Lead difluoride can be prepared by several methods. It is obtained by treating lead hydroxide or lead carbonate with hydrofluoric acid, followed by evaporation of the solution:



Alternatively, it is precipitated by adding hydrofluoric acid to a lead(II) salt solution; or adding potassium fluoride to lead nitrate solution:



Lead difluoride also can be directly synthesized from its elements, by the action of lead with fluorine.

**Analysis**

Elemental composition: Pb 84.50%, F 15.50%. The compound can be identified from its physical properties and x-ray measurement. Lead may be analyzed by various instrumental techniques (See Lead). Fluoride ion may be determined by dissolving a minute quantity of the compound in water (the compound is slightly soluble in water) and analyzing the solution by ion chromatography or by fluoride-ion selective electrode.

**Toxicity**

Slightly to moderately toxic by ingestion and subcutaneous routes. The oral LD<sub>50</sub> in rats is around 3,000 mg/kg.

**LEAD DIIODIDE**

[10101-63-0]

Formula: PbI<sub>2</sub>; MW 461.01

Synonyms: lead iodide; lead(II) iodide

**Uses**

Lead diiodide is used for recording optical images; for making gold spangles and mosaic gold for decorative purposes; in photographic emulsions; in mercury-vapor lamps; in asbestos brake linings; in far-infrared filters; in thermal batteries; in printing and recording papers; and in aerosols for cloud seeding.

**Physical Properties**

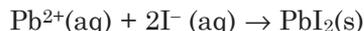
Yellow hexagonal crystals; density 6.16 g/cm<sup>3</sup>; melts at 402°C; vaporizes at 954°C; decomposes at 180°C when exposed to green light; slightly soluble in water (0.44 g/L at 0°C and 0.63 g/L at 20°C); K<sub>sp</sub> 8.49x10<sup>-9</sup> at 25°C; partially soluble in boiling water (4.1 g/L at 100°C); insoluble in ethanol; soluble in alkalis and alkali metal iodide solutions.

**Thermochemical Properties**

$\Delta H_f^\circ$	-41.94 kcal/mol
$\Delta G_f^\circ$	-41.50 kcal/mol
S°	41.79 cal/degree mol
C <sub>p</sub>	18.49 cal/degree mol

**Preparation**

Lead diiodide is prepared by mixing aqueous solutions of lead nitrate or lead acetate with an aqueous solution of potassium or sodium iodide or hydriodic acid, followed by crystallization. The product is purified by recrystallization.



**Analysis**

Elemental composition: Pb 44.94%, I 55.06%. An accurately weighted amount of the salt may be digested with nitric acid and the acid extract analyzed for lead by AA, ICP or other instrumental techniques. (See Lead.) A few milligrams of salt is dissolved in water and analyzed for iodide anion by ion chromatography. The solutions must be appropriately diluted for these analyses.

**Toxicity**

Lead diiodide is toxic if ingested. The symptoms are those of lead poisoning.

**LEAD DIOXIDE**

[1309-60-0]

Formula:  $\text{PbO}_2$ ; MW 239.20

Synonyms: lead(IV) oxide; lead peroxide; lead superoxide; brown lead oxide; plattnerite

**Occurrence and Uses**

Lead dioxide occurs in nature as the mineral plattnerite. It is used as an oxidizing agent in manufacturing dyes and intermediates. It also is used as a source of oxygen in matches, pyrotechnics, and explosives. In matches, the oxide is combined with amorphous phosphorus as an ignition surface. It also is used in making lead pigments, liquid polysulfide polymers and rubber substitutes. Lead dioxide electrodes are used in lead storage batteries in which lead dioxide accumulates on positive plates.

**Physical Properties**

Red tetragonal crystals or brown powder; density 9.64 g/cm<sup>3</sup>; decomposes on heating at 290°C; practically insoluble in water; also insoluble in alkalis; moderately soluble in hydrochloric acid and also, in nitric acid-hydrogen peroxide mixture; slowly dissolves in acetic acid.

**Thermochemical Properties**

$\Delta H_f^\circ$	-66.30 kcal/mol
$\Delta G_f^\circ$	-51.94 kcal/mol
$S^\circ$	16.40 cal/degree mol
$C_p$	15.44 cal/degree mol

**Preparation**

Lead dioxide is produced by oxidizing an alkaline slurry of lead monoxide with chlorine, sodium hypochlorite, or bleaching powder. Alternatively, it is obtained by passing chlorine into a hot aqueous suspension of lead sulfate and

magnesium hydroxide. The ionic reaction is:



It also is produced by electrolysis of acidic solutions of lead salts using a lead or platinum electrode. In such electrolytic process, lead dioxide is deposited on the anode of the cell.

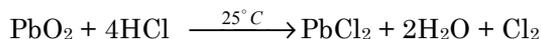
Insoluble powdered lead dioxide also may be obtained when lead tetroxide is heated with nitric acid:



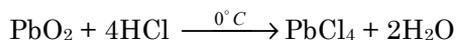
Lead dioxide also can be prepared by fusing lead monoxide with a mixture of sodium nitrate and sodium chlorate.

### Reactions

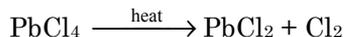
Lead dioxide exhibits amphoteric properties, reacting with both acids and alkalies. With acids, it forms both divalent and tetravalent salts, depending on acid strength and reaction temperature. Thus, it dissolves in concentrated hydrochloric acid at ambient temperature, forming lead(II) chloride with evolution of chlorine:



However, at 0°C some lead(IV) chloride also forms:



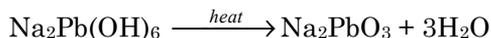
The tetrachloride decomposes to dichloride on warming:



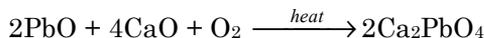
Lead dioxide reacts with alkalies forming various types of plumbates. Fusion with caustic soda or caustic potash yields orthoplumbates and metaplumbates, such as  $\text{Na}_4\text{PbO}_4$  or  $\text{Na}_2\text{PbO}_3$  (or the corresponding potassium salts). However, when dissolved in a concentrated aqueous solution of sodium or potassium hydroxide, the product is hydroxyplumbate:



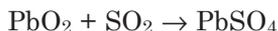
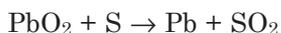
The hydroxyplumbate decomposes to metaplumbate on gentle heating:



When heated with quicklime in air, lead dioxide forms calcium plumbate:



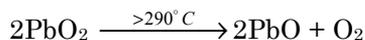
Lead dioxide is an oxidizing agent as well as a source of oxygen. It has many industrial applications. When heated with sulfur, the sulfur is oxidized to sulfur dioxide producing lead sulfate:



When heated with concentrated sulfuric acid, lead dioxide liberates oxygen, forming lead sulfate:



It decomposes to lead monoxide and oxygen when heated above 290°C:



### Analysis

Elemental composition: Pb 86.62%, O 13.38%. The compound may be identified by its physical properties and characterized by x-ray crystallography. Lead may be analyzed in the acid extract of the oxide by AA or ICP spectroscopy. It also may be analyzed by its oxidative properties. It liberates iodine from an acidic solution of potassium iodide, and the liberated iodine may be titrated against a standard solution of sodium thiosulfate using starch indicator (blue color decolorizes at the end point).

## LEAD HYDROXIDE

[19781-14-3]

Formula:  $\text{Pb}(\text{OH})_2$ ; MW 241.21

Synonym: plumbous hydroxide

### Uses

Lead hydroxide is used in making porous glass; in electrical-insulating paper; in electrolytes in sealed nickel-cadmium batteries; in recovery of uranium from seawater; and as a catalyst for oxidation of cyclododecanol.

### Physical Properties

White amorphous powder; density 7.41 g/cm<sup>3</sup>; dehydrates above 130°C and decomposes at 145°C; slightly soluble in water, 155 mg/L at 20°C;  $K_{\text{SP}}$  1.42x10<sup>-20</sup> at 25°C; soluble in dilute acids and alkalis; insoluble in acetone

## 472 LEAD MONOXIDE

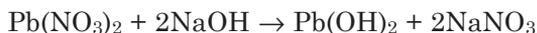
and acetic acid.

### Thermochemical Properties

$$\Delta G_f^\circ \quad -108.1 \text{ kcal/mol}$$

### Preparation

Lead hydroxide is precipitated by adding sodium hydroxide or potassium hydroxide to a solution of lead nitrate:



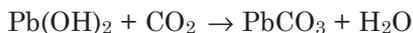
It also is produced by electrolysis of an alkali solution using lead anode. Lead hydroxide is formed on the anode.

### Reactions

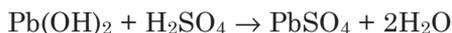
When heated at 145°C, lead hydroxide decomposes to lead monoxide:



It absorbs carbon dioxide forming lead carbonate:



It reacts with acids forming their lead salts:



### Analysis

Elemental composition: Pb 90.40%, H 0.29%, O 9.30%. The hydroxide is digested with nitric acid, diluted and analyzed for lead by AA, ICP or other instrumental technique (See Lead). A weighed amount of the salt is heated in an oven at 145°C and water lost is measured by gravimetry. The residue lead monoxide also may be analyzed by x-ray, or its lead content can be measured by various instrumental methods.

## LEAD MONOXIDE

[1317-36-8]

Formula: PbO; MW 223.30

Synonyms: lead(II) oxide; yellow lead oxide; litharge (red alpha modification of the oxide); massicot (yellow beta form)

### Uses

Lead monoxide has wide commercial applications. It is used in lead-sulfuric acid type storage battery plates; in optical and electrical glasses; in vitreous enamels, glazes, and fine tableware; in lead soaps for varnishes; as a vul-

canizing agent for rubber and plastics; and as a lubricant at high temperatures. An important application of this oxide involves its use as the starting material for producing various lead pigments as well as other compounds of commercial interest such as lead arsenate, lead acetate, and sodium plumbite. Also, lead monoxide is used in certain organic syntheses as a neutralizing agent.

### Physical Properties

The oxide exhibits two crystalline modifications, the reddish or orange-red alpha form, known as litharge, and the yellow beta form, massicot. The alpha form constitutes tetragonal crystals while the beta modification is a yellow amorphous powder of orthorhombic crystal structure. The alpha form is stable at ordinary temperatures, converting to the beta form when heated at 489°C; density 9.35 g/cm<sup>3</sup> (beta form); Moh's hardness 2 (alpha form); the oxide melts at 888°C; vaporizes at 1,472°C with decomposition; vapor pressure 1 torr at 943°C and 5 torr at 1,039°C; practically insoluble in water (the solubility of alpha form is 17 mg/L at 20°C and that of beta form 23 mg/L at 22°C); insoluble in ethanol; soluble in dilute nitric acid and alkalis.

### Thermochemical Properties

$\Delta H_f^\circ$	(alpha form)	-52.34 kcal/mol
$\Delta H_f^\circ$	(beta form)	-51.94 kcal/mol
$\Delta G_f^\circ$	(alpha form)	-45.15 kcal/mol
$\Delta G_f^\circ$	(beta form)	-44.91 kcal/mol
$S^\circ$	(alpha form)	15.89 cal/degree mol
$S^\circ$	(beta form)	16.42 cal/degree mol
$C_p$	(both forms)	10.95 cal/degree mol

### Production

Lead monoxide is obtained commercially by two processes, Barton process and the Ball Mill process. The Ball-Mill process involves reaction of molten lead with oxygen or air, and in the Barton process atomized molten lead is stirred in a mechanical furnace above 550°C. The molten metal splashed by the stirring paddle comes in contact with air fed into the cover of the furnace through a pipe, thus forming a mist of finely divided lead monoxide. The mist also contains a small amount of unreacted lead. The mist is passed through an upright shaft where a major portion of unreacted lead falls back into the furnace. It is then rapidly cooled and collected in condensing chambers. The crude product may contain 1 to 3% lead. It is finely ground and sold. The remaining lead in the crude product may be converted into the lead monoxide by stirring the molten mass in presence of air for several hours. The hot product is then cooled rapidly to a temperature below 300°C to prevent any formation of lead tetroxide, Pb<sub>3</sub>O<sub>4</sub>.

In an alternate process, a variation of the above method, molten lead is atomized in a shaft furnace. An air stream carries the very finely divided metal into the hot zone of the shaft furnace where the metal evaporates and oxidizes producing very finely divided lead monoxide. The product is passed

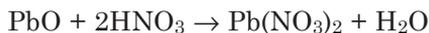
through the cold zone of the furnace and cooled rapidly. The product obtained is a yellow powdery material, the beta form of lead oxide, massicot, consisting of orthorhombic crystals.

The red lead oxide (the tetragonal alpha modification) is obtained by slow cooling of the lead monoxide melt. The solidified mass may contain the red alpha form of the oxide resulting from slow cooling of the melt, under an outer layer of yellow beta form that may result from the rapid cooling of the outer portion.

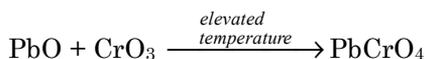
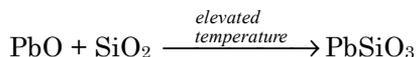
Lead monoxide also is produced by a modified Ball Mill process in which high purity lead balls placed in the mill are partially oxidized to produce black or grey oxide. Both the red and yellow form of the oxide may be prepared by alkaline dehydration of lead hydroxide,  $\text{Pb}(\text{OH})_2$ .

### Reactions

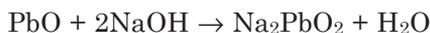
Lead monoxide is amphoteric in nature; i.e., the oxide exhibits both the acid (weakly acidic) and base characteristics. It dissolves in acids forming their corresponding salts:



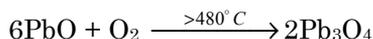
Similarly, it combines with silica and chromium(VI) oxide at elevated temperatures, forming lead silicate and lead chromate, respectively:



It also reacts with alkalis, forming the plumbite ion,  $\text{PbO}_2^{2-}$ . In aqueous alkalis it dissolves slowly forming hydroxyplumbites; i.e.,  $\text{Na}_2\text{Pb}(\text{OH})_4$ , which decomposes to plumbite. The overall reaction is:



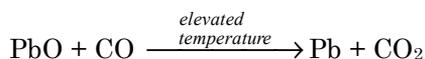
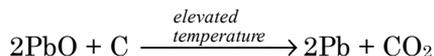
When heated at 450–500°C in air or oxygen in a reverberatory furnace, lead monoxide is oxidized to lead tetroxide. However, other oxides or their mixtures having varying compositions may also form. The reaction is slow and gradual above 430°C.



When heated with lead dioxide, at 250°C, the same product, lead tetroxide is obtained:



The oxide can be reduced to metallic lead by hydrogen, carbon, carbon monoxide and other reducing agents when heated at elevated temperatures. Such reduction with carbon or carbon monoxide is carried out at about 1000°C in a blast furnace to produce lead metal:



### Analysis

Elemental composition: Pb 92.83%, O 7.17%. The oxide may be characterized by x-ray crystallography, and physical properties. Lead may be analyzed in the acid extract by AA, ICP and other instrumental techniques (See Lead).

### Toxicity

The monoxide is moderately toxic by ingestion and inhalation of dust. The symptoms are those of lead poisoning.

## LEAD NITRATE

[10099-74-8]

Formula:  $\text{Pb}(\text{NO}_3)_2$ ; MW 331.21

### Uses

Lead nitrate is used as a mordant in dyeing and printing cotton; as a flotation agent to remove titanium from clays; to prepare several lead salts; in electrolytic refining for production of lead; in photothermography; as a heat stabilizer in nylon; as a catalyst for polyester synthesis; in delustering of rayon; in recovery of precious metals from cyanide solutions; in making electroluminescent mixtures; and as an analytical standard for lead. Lead nitrate also is used in matches, pyrotechnics and explosives, where it is a source of oxygen.

### Physical Properties

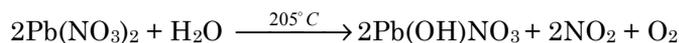
Colorless cubic or monoclinic crystals; refractive index 1.782; density 4.53 g/cm<sup>3</sup> at 20°C; decomposes at 470°C; soluble in cold water; very soluble in boiling water 127 g/100 mL at 100°C; also soluble in caustic soda, caustic potash and ammonia solution, and moderately soluble in alcohol.

### Preparation

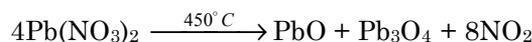
Lead nitrate is prepared by dissolving lead metal, lead monoxide or lead carbonate in excess dilute nitric acid followed by evaporation of and/or cooling the solution for crystallization.

**Reactions**

Thermal dissociation above 205°C yields basic lead nitrate, nitrogen dioxide and oxygen:



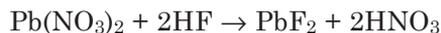
When heated above 450°, it decomposes to lead monoxide and lead tetroxide:



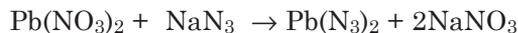
Reaction with sodium carbonate and powdered tellurium yields lead telluride, PbTe.

Reaction with sodium selenate yields lead selenate, PbSeO<sub>4</sub>. Similarly, with sodium selenite or selenious acid, the product is lead selenite, PbSeO<sub>3</sub>.

When its aqueous solution is mixed with hydrofluoric acid, lead fluoride precipitates out:



Reaction with sodium azide yields lead azide:

**Analysis**

Elemental composition: Pb 62.55%, N 8.46%, O 28.98%. The aqueous solution may be analyzed for lead by various instrumental techniques (See Lead). The nitrate ion may be identified by a nitrate ion-selective electrode or by ion chromatography following appropriate dilution of the solution. The compound may be identified in crystalline forms by x-ray and by its physical properties.

**Toxicity**

The toxic effects are greater than other lead salts because lead nitrate is more soluble. Moderately toxic by ingestion and other routes of exposure. The compound also is an irritant to eye, skin, and mucous membranes.

**LEAD SULFATE**

[7446-14-2]

Formula: PbSO<sub>4</sub>; MW 303.26

**Occurrence and Uses**

Lead sulfate occurs in nature as the mineral, anglesite. It is an essential component of lead-sulfuric acid storage batteries and forms during discharge

cycles. It is used as an additive to stabilize clay soil for construction. Other applications are in photography and as a pigment.

### Physical Properties

White monoclinic or rhombic crystals; refractive index 1.877; density 6.20 g/cm<sup>3</sup>; melts at 1,170°C; very slightly soluble in water, 42.5 mg/L at 25°C;  $K_{SP} 1.82 \times 10^{-8}$ ; sparingly soluble in hydrochloric and nitric acids; slightly soluble in dilute sulfuric acid, more soluble in concentrated sulfuric acid; insoluble in alcohol; soluble in caustic soda and ammonium salts solutions.

### Thermochemical Properties

$\Delta H_f^\circ$	-219.9 kcal/mol
$\Delta G_f^\circ$	-194.4 kcal/mol
$S^\circ$	35.5 cal/degree mol
$C_p$	24.7 cal/degree mol

### Preparation

Lead sulfate precipitates when an aqueous solution of lead nitrate or other soluble salt of lead is treated with sulfuric acid.

Alternatively, lead sulfate may be prepared by treating lead oxide, hydroxide, or carbonate with concentrated sulfuric acid under warm condition.

It also is produced when lead sulfide is roasted in air.

### Analysis

Elemental composition: Pb 68.32%, S 10.57%, O 21.10%. the solid crystalline powder or the mineral anglesite may be characterized by x-ray techniques and physical properties. Lead can be analyzed in the solid compound or its nitric acid extract by various instrumental techniques (See Lead).

### Toxicity

Low to moderate toxicity by ingestion. Irritant action on eye, skin, and mucous membranes.

## LEAD SULFIDE

[1314-87-0]

Formula: PbS; MW 239.30

Synonyms: galena; lead glance

### Occurrence and Uses

Lead sulfide occurs in nature as the mineral galena. Most lead comes from this ore. Additionally, lead sulfide has several industrial applications. It is used in infrared detectors; transistors; photoconductive cells; high temperature lubricants; and for glazing earthenware. It also is used as a catalyst in petroleum refining for removal of mercaptans from petroleum distillates.

**Physical Properties**

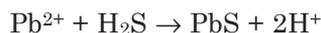
Black powder or cubic crystal; refractive index 3.91; density 7.60 g/cm<sup>3</sup>; Moh's hardness 2.5; melts at 1,118°C; vapor pressure 1 torr at 852°C and 5 torr at 928°C; very slightly soluble in water (124 mg/L at 20°C);  $K_{SP}$   $9.04 \times 10^{-29}$  at 25°C; soluble in acids.

**Thermochemical Properties**

$\Delta H_f^\circ$	-24.0 kcal/mol
$\Delta G_f^\circ$	-23.6 kcal/mol
$S^\circ$	21.8 cal/degree mol
$C_p$	11.83 cal/degree mol

**Preparation**

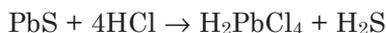
Lead sulfide occurs naturally as the mineral galena. It can be prepared in the laboratory as a black precipitate by passing hydrogen sulfide through a dilute acid solution of inorganic lead salt, such as lead nitrate or lead acetate:



It also is obtained by direct combination of elements by heating metallic lead with sulfur vapors.

**Reactions**

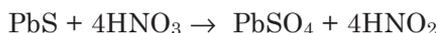
Lead sulfide decomposes in excess concentrated hydrochloric acid liberating hydrogen sulfide and probably forming chloroplumbic acid in solution:



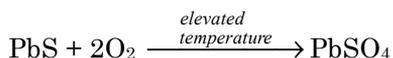
Two types of reactions occur with nitric acid depending on the concentration of the acid. Lead sulfide dissolves in dilute nitric acid, oxidizing to elemental sulfur:

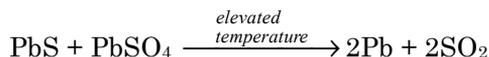
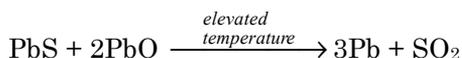
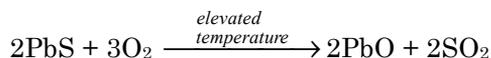


However, treatment with concentrated nitric acid yields lead(II) sulfate:



Lead sulfide also undergoes various oxidation reactions at elevated temperatures that occur in a reverberatory furnace, during the production of lead from galena. Sulfur dioxide and lead sulfate are formed as intermediate products. Some typical reactions are as follows:





When roasted in an air blast furnace, basic lead sulfate,  $\text{PbO} \cdot \text{PbSO}_4$  (also known as sublimed white lead), is formed.

### Analysis

Elemental composition: Pb 86.60%, S 13.40%. Both mineral and synthetic forms can be identified by x-ray measurements. Lead can be analyzed by various instrumental techniques after digestion with nitric acid and appropriate dilution of the acid extract (See Lead).

## LEAD TETRAACETATE

[546-67-8]

Formula:  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_4$ ; MW 443.38

Synonyms: plumbic acetate; lead(IV) acetate

### Uses

Lead tetraacetate is used as a highly selective oxidizing agent in organic synthesis. This includes oxidation of glycols into aldehydes, preparation of cyclohexyl acetate, production of oxalic acid, and in structural analysis of sugars.

### Physical Properties

Colorless monoclinic crystals; turns pink; unstable in air; density 2.228  $\text{g/cm}^3$  at 17°C; melts at 175°C; decomposes in cold water and ethanol; soluble in chloroform, benzene, nitrobenzene, and hot glacial acetic acid; also soluble in concentrated hydrochloric acid.

### Preparation

Lead tetraacetate is prepared by dissolving lead tetroxide in warm glacial acetic acid followed by cooling. On cooling, the tetraacetate crystallizes out while lead acetate remains in the solution:



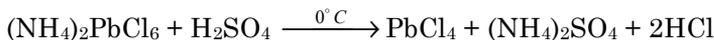
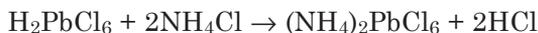
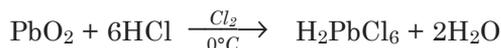
### Preparation

Lead tetrachloride may be prepared by dissolving lead dioxide in cold concentrated hydrochloric acid at 0°C:



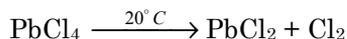
However, in the above method some amount of lead dichloride may form, especially if the temperature is above 0°C.

The preferred preparation method is to introduce chlorine into the solution while dissolving lead dioxide in cold concentrated HCl. This prevents decomposition of PbCl<sub>4</sub> to PbCl<sub>2</sub> and enhances the formation of chloroplumbic acid, H<sub>2</sub>PbCl<sub>6</sub> in solution. Addition of ammonium chloride precipitates out yellow ammonium chloroplumbate, (NH<sub>4</sub>)<sub>2</sub>PbCl<sub>6</sub>, which is filtered out. The yellow precipitate, on treatment with cold concentrated sulfuric acid, forms lead tetrachloride, which separates out as a yellow oily liquid. The reactions are:

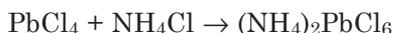


### Reactions

Lead tetrachloride decomposes at 20°C, forming lead dichloride and evolving chlorine:



Reaction with ammonium chloride yields yellow precipitate of the complex salt, ammoniumhexachloroplumbate(IV):



The tetrachloride rapidly hydrolyzes in water forming lead dioxide:



### Analysis

Elemental composition: Pb 59.37%, Cl 40.63%. The compound is hydrolyzed in water to PbO<sub>2</sub>, which is separated, digested with nitric acid, diluted, and analyzed for lead. The aqueous solution containing the hydrolysis product HCl is determined by acid-base titration. The chloride ion is measured by an electrode or ion chromatography, or by titration with a standard solution of

silver nitrate using potassium chromate indicator. The compound liberates chlorine gas at ordinary temperatures, which may be determined from its physical properties or by GC-TCD or collected in water and measured by colorimetry.

## LEAD TETRAETHYL

[78-00-2]

Formula:  $\text{Pb}(\text{C}_2\text{H}_5)_4$ ; MW 323.44

Synonyms: tetraethyllead; tetraethylplumbane; TEL

### Uses

Lead tetraethyl was used extensively as an additive to gasoline to prevent "knocking" in motors. Its use, however, is reduced drastically because of environmental pollution.

### Physical Properties

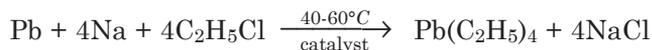
Colorless liquid; burns with orange flame with green margin; refractive index 1.5198; density 1.653 g/mL at 20°C; insoluble in water; slightly soluble in ethanol; soluble in benzene, toluene, gasoline, and petroleum ether.

### Thermochemical Properties

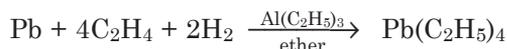
$\Delta H_f^\circ$	(liq)	-12.6 kcal/mol
$\Delta H_f^\circ$	(gas)	-26.2 kcal/mol

### Preparation

Lead tetraethyl is prepared by heating ethyl chloride in the presence of a catalyst in an autoclave at 40 to 60°C with an alloy of lead and sodium:



Also, it can be prepared by the reaction of lead with ethylene and hydrogen in the presence of Ziegler catalyst, triethylaluminum:



### Analysis

Elemental composition: Pb 64.06%, C 29.70%, H 6.23%. Tetraethyl lead is dissolved in benzene or toluene, diluted appropriately, and analyzed by GC/MS. The ethyl group may be determined by NMR spectroscopy.

### Toxicity

Tetraethyl lead is a highly toxic compound manifesting both acute and chronic effects. These effects are insomnia, hypotension, hypothermia, tremor,

weight loss, hallucination, nausea, convulsion and coma. LD<sub>50</sub> oral (rats): 12 mg/kg

## LEAD TETRAFLUORIDE

[7783-59-7]

Formula: PbF<sub>4</sub>; MW 283.18

### Uses

Lead tetrafluoride is used as a fluorinating agent for hydrocarbons.

### Physical Properties

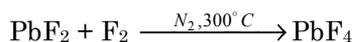
White tetragonal crystals; density 6.7 g/cm<sup>3</sup>; melts at about 600°C; hydrolyzes readily when exposed to moist air.

### Thermochemical Properties

$\Delta H_f^\circ$  -225.10 kcal/mol

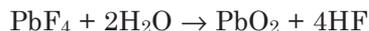
### Preparation

The tetrafluoride is obtained by fluorination of lead difluoride. The method involves passing a mixture of fluorine and nitrogen or carbon dioxide over lead difluoride at 300°C.



### Reactions

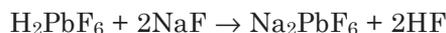
Lead tetrafluoride is readily hydrolyzed by moisture, turning brown and forming lead dioxide:



The tetrafluoride also hydrolyzes in dilute hydrofluoric acid. However, in concentrated acid, it forms fluoplumbic acid, H<sub>2</sub>PbF<sub>6</sub>:



When an alkali metal fluoride or ammonium fluoride is added to a solution of lead tetrafluoride in concentrated hydrofluoric acid, salts of fluoplumbic acid are obtained:



### Analysis

Elemental composition: Pb 73.16%, F 26.84%. A small measured quantity of the compound is hydrolyzed in water and the aqueous solution is appropriately diluted and analyzed for fluoride ion, either by ion-specific electrode or

by ion chromatography. The solution is digested with nitric acid and analyzed for lead by AA, ICP, or other instrumental methods (See Lead).

## LEAD TETROXIDE

[1314-41-6]

Formula:  $\text{Pb}_3\text{O}_4$ ; MW 685.60

Synonyms: red lead; minium; trilead tetroxide; lead orthoplumbite; mineral red; Paris red.

### Uses

Lead tetroxide has many applications. The most important use is in paint and storage-batteries. It is used as a pigment in corrosion-protecting paints for steel surfaces. It also is used in positive battery plates; in colored glasses and ceramics; in glass sealants for television picture tubes; in propellants and explosives; in radiation shields for x-rays and gamma rays; in the vulcanization of rubber; in glass-writing pencils; in adhesives for tire cords; in foaming agents and waterproofing materials; in plasters and ointments; in lead dioxide matches; and as a catalyst for oxidation of carbon monoxide in exhausts.

### Physical Properties

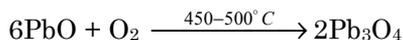
Bright-red crystalline substance or amorphous powder; density  $9.1 \text{ g/cm}^3$ ; decomposes on heating to  $500^\circ\text{C}$ , melts at  $830^\circ\text{C}$  under pressure and oxygen; insoluble in water and alcohol; soluble in glacial acetic acid, hot hydrochloric acid, and a dilute nitric acid-hydrogen peroxide mixture.

### Thermochemical Properties

$\Delta H_f^\circ$	-171.7 kcal/mol
$\Delta G_f^\circ$	-143.7 kcal/mol
$S^\circ$	50.5 cal/degree mol
$C_p$	35.1 cal/degree mol

### Preparation

Lead tetroxide is made by heating lead monoxide in the presence of air at temperatures between  $450$  to  $500^\circ\text{C}$ . The temperature should be maintained below  $500^\circ\text{C}$ , above which the tetroxide decomposes.

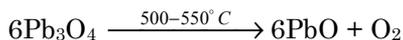


Alternatively, the tetroxide may be prepared by heating a mixture of lead monoxide and lead dioxide at  $250^\circ\text{C}$ :

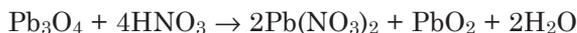


**Reactions**

When heated above 550°C, the tetroxide decomposes to monoxide, evolving oxygen:

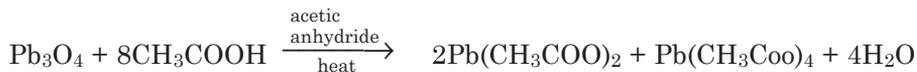


Lead tetroxide reacts with dilute nitric acid forming lead nitrate and precipitating lead dioxide:



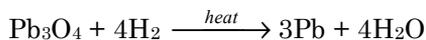
The above reaction may be explained by assuming lead tetroxide as formally equivalent to plumbus plumbate having a structure  $\text{Pb}_2^{\text{II}}[\text{Pb}^{\text{IV}}\text{O}_4]$  in which  $\text{Pb}^{2+}$  dissolves in dilute nitric acid forming lead(II) nitrate while  $\text{Pb}^{4+}$  precipitates out as lead(IV) oxide.

Lead tetroxide reacts with anhydrous acetic acid at 80°C producing lead(II) acetate and lead(IV) acetate. Alternatively, the tetroxide is added into a mixture of glacial acetic acid and acetic anhydride and heated gently:



On cooling, the tetraacetate crystallizes, leaving diacetate in the solution. Acetic anhydride is added to react with water produced in the reaction to form acetic acid and thus prevent hydrolysis.

Lead tetroxide can be reduced to metallic lead when heated with reducing agents, such as hydrogen, carbon, or carbon monoxide:

**LEAD TRIOXIDE**

[1314-27-8]

Formula:  $\text{Pb}_2\text{O}_3$ ; MW 462.40

Synonyms: lead sesquioxide; dilead trioxide; plumbous metaplumbate

**Uses**

Lead trioxide is a catalyst for oxidation of carbon monoxide in exhaust gases. Other uses are vulcanizing neoprene rubber; fireproofing plastics; detecting radiation; and manufacturing high-purity diamonds.

**Physical Properties**

Orange-yellow amorphous powder; decomposes at 370°C; insoluble in cold water; decomposes in hot water and acids.

**Thermochemical Properties**

$S^\circ$	36.3 cal/degree mol
$C_p$	25.7 cal/degree mol

**Preparation**

Lead trioxide is prepared by adding sodium hypochlorite or bromine to an aqueous solution of sodium plumbite.

**Reaction**

When heated in air at 370°C, the trioxide converts to tetroxide,  $Pb_3O_4$ . It dissociates to lead monoxide on heating at 530°C. It decomposes in acids forming lead dioxide and the corresponding salts of the acids. With concentrated sulfuric acid, the products are lead dioxide and lead sulfate with evolution of oxygen:

**Analysis**

Elemental composition: Pb 89.62%, O 10.38%. The composition of this oxide may be determined from analysis of lead in acid extract. The compound may be characterized by x-ray analysis and from physical properties.

**LITHIUM**

[7439-93-2]

Symbol Li; atomic number 3; atomic weight 6.941; a Group IA (Group 1) alkali metal element; lightest metal; electron configuration:  $1s^2 2s^1$ ; atomic radius 1.225Å; ionic radius  $Li^+$  0.59Å (for CN 4), and 0.76Å (for CN 6); first ionization potential 5.392eV; valence +1; two naturally occurring stable isotopes, Li-7 (92.4%) and Li-6 (7.6%), and three radioactive isotopes, Li-5, Li-8, and Li-9.

**History, Occurrence, and Uses**

Lithium was first discovered in 1817 by Arfvedsen in its silicoaluminate mineral, petalite. However, the metal first was isolated from its mineral by Bunsen and Matthiesen in 1855. Lithium is distributed widely in nature. Its concentration in the earth's crust is 20 mg/kg, and in seawater is 0.18mg/L. It is found in many chloride brines at varying but significant amounts. The principal minerals are:

spodumene (spar):  $LiAlSi_2O_6$  (theoretical  $Li_2O$  content 8.03%)

petalite:  $LiAlSi_4O_{10}$  (theoretical  $Li_2O$  content 4.88%)

lepidolite (lithium mica):  $K(Li,Al)_3(Si,Al)_4O_{10}(F,OH)_2$  (varying compositions; theoretical  $Li_2O$  content 3–4%)

amblygonite:  $\text{LiAlFPO}_4$  (theoretical  $\text{Li}_2\text{O}$  content >8%)

hectorite:  $\text{Na}_{0.33}(\text{Mg},\text{Li})_3\text{Si}_4\text{O}_{10}(\text{F},\text{OH})_2$  (theoretical  $\text{Li}_2\text{O}$  content 0.7–1.3%)

The metal has numerous industrial applications. It is used to make high-energy lithium batteries. Lithium and its aluminum alloys are used as anodes in non-aqueous solid-state batteries. Also, many of its salts are used as electrolytes in these batteries. Another major application is in metallurgy. Lithium is alloyed with lead, magnesium, aluminum and other metals. Its alloy Bahnmetall is used for wheel bearings in railroad cars, and its magnesium alloy is used in aerospace vehicles. Probably the most important applications of lithium are in preparative chemistry. It is the starting material to prepare lithium hydride, amide, nitride, alkyls and aryls. Lithium hydrides are effective reducing agents. The alkyls are used in organic syntheses.

### Physical Properties

Soft silvery-white metal; body-centered cubic structure; density 0.531  $\text{g}/\text{cm}^3$ ; burns with a carmine-red flame, evolving dense white fumes; melts at 180.54°C; vaporizes at 1,342°C; vapor pressure 1 torr at 745°C and 10 torr at 890°C; electrical resistivity 8.55 microhm-cm at 0°C and 12.7 microhm-cm at 100°C; viscosity 0.562 centipoise at 200°C and 0.402 centipoise at 400°C; reacts with water; soluble in liquid ammonia forming a blue solution.

### Thermochemical Properties

$\Delta H_f^\circ$ (cry)	0.0
$\Delta H_f^\circ$ (gas)	38.09 kcal/mol
$\Delta G_f^\circ$ (gas)	30.28 kcal/mol
$S^\circ$ (cry)	6.96 cal/degree mol
$S^\circ$ (gas)	33.14 cal/degree mol
$C_p$ (cry)	5.92 cal/degree mol
$C_p$ (gas)	4.97 cal/degree mol
$\Delta H_{\text{fus}}$	0.716 kcal/mol
$\Delta H_{\text{vap}}$	35.34 kcal/mol
Thermal conductivity at 0°C	0.17 cal/sec/cm/cm <sup>2</sup> /°C
Coefficient of linear expansion at 20°C	56x10 <sup>-6</sup> /°C

### Production

Lithium is obtained primarily from its ore, spodumene. Another important source is natural brine found in many surface and ground waters, from which the metal also is produced commercially.

The first production step involves recovery of the metal from spodumene. The naturally occurring ore, alpha-spodumene is heated in a brick-lined rotary kiln at a temperature between 1,075 to 1,100°C. This converts the alpha form to a more reactive form, beta-spodumene. The beta form is heated in a rotary kiln at 250°C with an excess of 93% sulfuric acid. The metal reacts with acid forming lithium sulfate. The kiln discharge is leached with water to separate water-soluble lithium sulfate from several impurity metals. Aqueous solution containing excess sulfuric acid is then neutralized by treatment with an excess of ground calcium carbonate (limestone). The solution is filtered to

remove unreacted limestone along with the products calcium sulfate and the sulfates of aluminum and iron. The solution containing saturated calcium sulfate and magnesium ions from limestone are then treated with calcium hydroxide upon which magnesium precipitates as hydroxide. The magnesium hydroxide is filtered from the solution. Addition of sodium carbonate to the filtrate precipitates calcium carbonate leaving lithium sulfate behind in the solution. The pH of the solution is then adjusted to between 7 and 8 with sulfuric acid. The solution is concentrated by evaporation after which it is treated with 28% sodium carbonate solution. Upon heating at 90 to 100°C, lithium carbonate precipitates. The precipitate is separated by centrifugation and washed and dried for further treatment.

Alternatively, limestone may be used instead of sulfuric acid to recover lithium from spodumene. Such recovery processes, known as alkaline methods, involve heating the ore with a mixture of ground limestone and calcium sulfate or chloride to form lithium sulfate or chloride. Leaching the kiln discharge with water yields an aqueous solution of lithium sulfate or chloride.

Several ion-exchange methods are also known that offer efficient recovery of lithium from its ores. In such processes, ore is heated with an acid, or its sodium or potassium salt, at moderate temperatures between 100 to 350°C. Often an aqueous solution of sodium or potassium salt such as sodium carbonate is employed which is heated with the ground ore in a steam autoclave. Lithium ions are liberated into aqueous solution from the silicate complex, exchanging hydrogen, sodium or potassium ions.

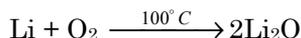
Lithium may be recovered from natural chloride brines. Such recovery processes may require additional steps depending on the magnesium and calcium content of the brine. The process involves evaporation of brine, followed by removal of sodium chloride and interfering ions such as calcium and magnesium. Calcium is removed by precipitation as sulfate while magnesium is removed by treating the solution with lime upon which insoluble magnesium hydroxide separates out. Addition of sodium carbonate to the filtrate solution precipitates lithium carbonate.

Lithium metal is produced commercially by electrolysis of a fused eutectic mixture of lithium chloride-potassium chloride (45% LiCl) at 400 to 450°C. The eutectic mixture melts at 352°C in comparison to the pure LiCl melting at 606°C. Also, the eutectic melt is a superior electrolyte to LiCl melt. (Landolt, P.E. and C. A. Hampel. 1968. *Lithium*. In *Encyclopedia of Chemical Elements*. C. A. Hampel, Ed. Reinhold Book Corp. New York.) Electrolysis is carried out using graphite anodes and steel cathodes. Any sodium impurity in lithium chloride may be removed by vaporizing sodium under vacuum at elevated temperatures. All commercial processes nowadays are based on electrolytic recovery of the metal. Chemical reduction processes do not yield high purity-grade metal. Lithium can be stored indefinitely under airtight conditions. It usually is stored under mineral oil in metal drums.

## Reactions

Lithium metal is highly reactive but less so than other alkali metals. Its chemical properties, however, are more like those of the alkaline earth metals.

At ordinary temperatures, lithium does not react with dry oxygen. However, it reacts above 100°C, forming lithium oxide, Li<sub>2</sub>O:

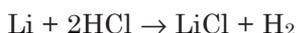


The metal ignites in air near its melting point, burning with intense white flame, forming Li<sub>2</sub>O.

Lithium reacts with water forming lithium hydroxide with evolution of hydrogen:

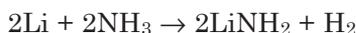


The reaction is violent when lithium metal is in finely divided state. Lithium reacts violently with dilute acids, liberating hydrogen:



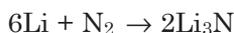
Reaction with cold concentrated sulfuric acid is slow.

The metal dissolves in liquid ammonia, forming a blue solution, lithium amide, LiNH<sub>2</sub>:



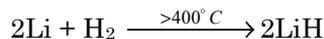
The same product also is obtained from ammonia gas.

Unlike other alkali metals, lithium reacts with nitrogen in the presence of moisture at ordinary temperatures, forming the black lithium nitride, Li<sub>3</sub>N:

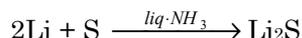


The above reaction is exothermic.

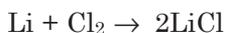
Lithium reacts with hydrogen at red heat forming lithium hydride:



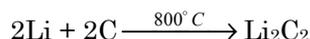
Reactions with sulfur and selenium in liquid ammonia yield lithium sulfide and selenide, respectively:



The metal combines with chlorine and other halogens, forming their halides:



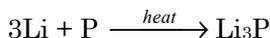
When heated with carbon at 800°C, the product is lithium carbide:



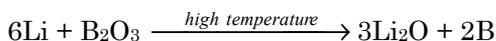
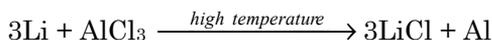
The metal reacts with carbon dioxide at elevated temperatures, forming lithium carbonate,  $\text{Li}_2\text{CO}_3$ .

Lithium forms alloys with several metals including aluminum, calcium, copper, magnesium, mercury, sodium, potassium, silver, tin and zinc.

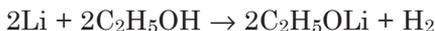
It combines with phosphorus, arsenic and antimony on heating, forming their binary salts:



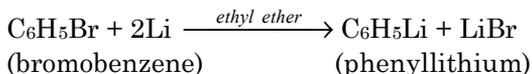
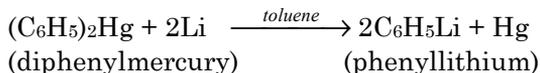
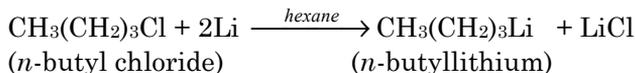
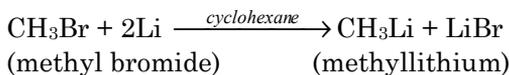
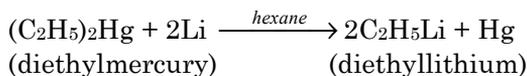
The metal behaves as a reducing agent at high temperatures. It reduces aluminum chloride to aluminum and boron oxide to boron:



Lithium liberates hydrogen from ethanol, forming lithium ethoxide:



Several organolithium compounds have important applications in organic syntheses. These may be readily synthesized by reactions of lithium with organics. The metal reacts with alkyl or aryl halides or mercury alkyls or aryls to produce alkyl or aryl lithium. Some examples are:



### Analysis

Lithium metal can be determined by several instrumental methods, including flame AA, ICP-AES, ICP-MS, x-ray fluorescence and flame emission pho-

tometry. Flame AA measurement may be done at the wavelength 670.8 nm in the absorption mode using air-acetylene flame—or in the emission mode at the same wavelength.

### Hazard

Lithium metal is less reactive than other alkali metals. However, violent explosions may occur when lithium is combined with halogenated hydrocarbons, such as chloroform or carbon tetrachloride. Violent reactions can occur with many other substances at high temperatures.

## LITHIUM ALUMINUM HYDRIDE

[16853-85-3]

Formula:  $\text{LiAlH}_4$ ; MW 37.95; ionic bond between  $\text{Li}^+$  and  $\text{AlH}_4^-$  ions.

Synonyms: lithium tetrahydroaluminate; aluminum lithium hydride; lithium aluminum tetrahydride

### Uses

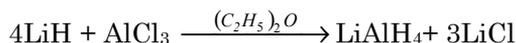
Lithium aluminum hydride is among the most important industrial reducing agents. It is used extensively in organic syntheses and also in catalytic hydrogenation.

### Physical Properties

White crystalline powder when pure; monoclinic crystals; grey in the presence of aluminum impurity; stable below 120°C in dry air; turns grey on standing; hygroscopic; density 0.917 g/cm<sup>3</sup>; melts at 190°C (decomposes); reacts with water and alcohols; soluble in diethylether and tetrahydrofuran (about 30 and 13 g/100g, respectively at 25°C; also soluble in dimethylcellosolve; sparingly soluble in dibutylether; slightly soluble in dioxane (1g/L) and practically insoluble in hydrocarbons; can be solubilized in benzene by crown ether.

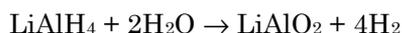
### Preparation

Lithium aluminum hydride is prepared by reaction of lithium hydride with aluminum chloride in diethylether:



### Reactions

Lithium aluminum hydride reacts violently with water evolving hydrogen. About 2.36L H<sub>2</sub> is evolved per 1 g of the compound at NTP.



Also, it reacts with alcohols evolving hydrogen:

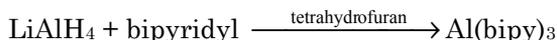
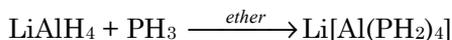
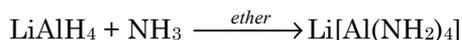


Reactions with metal chlorides yield metal hydrides:



It also reduces sodium methoxide,  $\text{NaOCH}_3$  into sodium hydride,  $\text{NaH}$ .

Lithium aluminum hydride reacts with many inorganic and organic neutral ligands, forming coordinated alumina complexes associated with lithium ions:

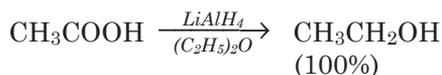


Almost all organic functional groups except for olefinic double bonds are reduced by lithium aluminum hydride. It reduces acids, esters, acid chlorides, amides, imides, imines, nitriles, nitroorganics, epoxides, and lactones.

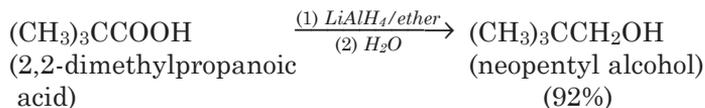
Most carboxylic acids are completely reduced to primary alcohols.



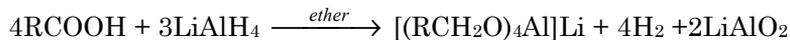
Reduction of acetic acid to ethanol is complete:



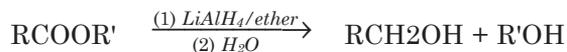
Carboxylic acids containing tertiary carbon atoms yield a lower product.



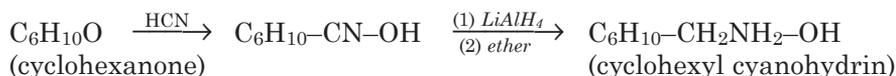
A balanced equation for conversion of carboxylic acid to alcohol and other products is:



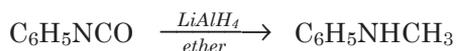
Esters are reduced to alcohols, the products depending upon alkyl groups in the ester:



Another synthetic reaction involves the reduction of cyanohydrins to yield  $\beta$ -amino alcohols:



Esters are completely reduced to alcohols; while unsaturated esters are converted to unsaturated alcohols. Other reduction reactions include conversion of phenyl isocyanate to N-methylaniline:



and dechlorination of polyvinyl chloride at 100°C in tetrahydrofuran.

### Hazard

Lithium aluminum hydride is a flammable substance. It ignites spontaneously on grinding and reacts violently with water and many organic substances. Diethyl ether, tetrahydrofuran or another suitable solvent should be used in its synthetic applications. Dry or powdered limestone is an appropriate fire extinguishing agent.

## LITHIUM AMIDE

[7782-89-0]

Formula:  $\text{LiNH}_2$ ; MW 22.96

### Uses

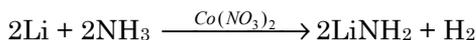
Lithium amide is used in synthesis of histamine and analgesic drugs. The compound also is used in many organic synthetic reactions including alkylation of ketones and nitriles, Claisen condensation, and in synthesis of antioxidants and acetylenic compounds.

### Physical Properties

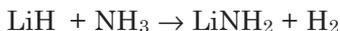
Colorless needles; tetragonal structure; density 1.178 g/cm<sup>3</sup> at 17.5°C; melts around 375°C; starts to decompose at 320°C; decomposes at 400°C; soluble in cold water; decomposes in hot water; slightly soluble in ethanol and liquid ammonia; insoluble in benzene and ether.

### Preparation

Lithium amide is obtained by dissolution of lithium metal in liquid ammonia. The reaction is slow, but may be catalyzed by cobalt nitrate:



It also is obtained by passing gaseous ammonia over lithium hydride:

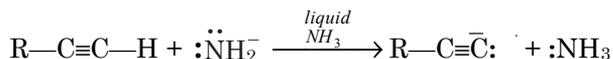


### Reactions

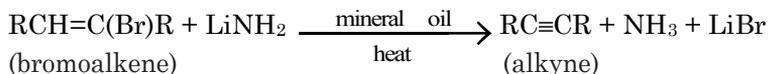
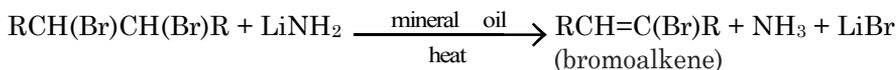
Lithium amide decomposes to imide when heated above 400°C:



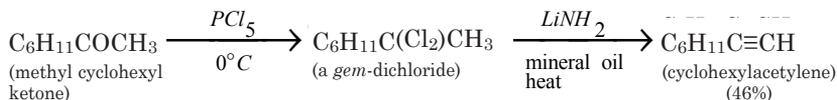
It is used in several organic syntheses. Some of these synthetic reactions are based on the mechanism that the terminal alkynes react with the stronger base, the anion, forming the weaker conjugate base:



It converts *vic* dibromide to bromoalkene and then alkyne:



Ketones can be converted into alkynes:



## LITHIUM BOROHYDRIDE

[16949-15-8]

Formula:  $\text{LiBH}_4$ ; MW 21.78

Synonyms: lithium tetrahydroborate; lithium boron hydride

**Uses**

Lithium borohydride is used as a strong reducing agent. Its principal applications are in organic syntheses for reducing carbonyl groups such as aldehydes, ketones, and esters. It also is used for selectively reducing a carbonyl group in the presence of a nitrile group. Such selective reduction cannot be achieved with lithium aluminum hydride, which is a much stronger reducing agent. The compound also is used to detect free carbonyl groups in proteins and peptides.

**Physical Properties**

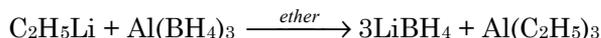
White orthorhombic crystals; density 0.67 g/cm<sup>3</sup>; decomposes in moist air; melts at 268°C; decomposes at 380°C; reacts with water; dissolves in ether, tetrahydrofuran, and diethylamine; solubility in ether, 25g/L at 25°C.

**Thermochemical Properties**

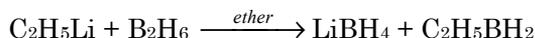
$\Delta H_f^\circ$	-45.60 kcal/mol
$\Delta G_f^\circ$	-29.90 kcal/mol
$S^\circ$	18.13 cal/degree mol
$C_p$	19.73 cal/degree mol

**Preparation**

Lithium borohydride is prepared by reacting ethyllithium with aluminum borohydride:



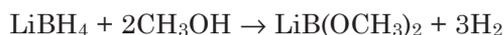
Alternatively, the compound may be obtained by the reaction of ethyllithium with diborane:

**Reactions**

Lithium borohydride reacts with water with liberation of hydrogen:

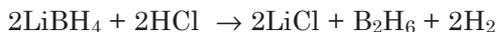


Reaction with methanol yields lithium boromethoxide and hydrogen:



Reaction with hydrogen chloride yields diborane, lithium chloride and

hydrogen:



Reactions with oxidizing agents are violent.

### Analysis

Elemental composition: Li 31.85%, B 49.66%, H 18.50%. The compound is dissolved in water cautiously and the evolved hydrogen is measured by GC using a TCD. The aqueous solution is treated with nitric acid and the diluted nitric acid extract is analyzed for lithium by atomic absorption or emission spectroscopy (See Lithium).

## LITHIUM BROMIDE

[7550-35-8]

Formula: LiBr; MW 86.85; forms stable hydrates, LiBr·H<sub>2</sub>O, LiBr·2H<sub>2</sub>O, and LiBr·3H<sub>2</sub>O.

### Uses

Lithium bromide is used in absorption, refrigeration and air-conditioning systems. A highly concentrated solution of the salt is an efficient absorbent of water vapor. The vapor pressure of such solution is very low. Other applications include the use of the salt as a swelling agent for wool, hair and other organic fibers; as a catalyst in dehydrohalogenation reactions; and as a sedative and hypnotic in medicine.

### Physical Properties

White cubic crystals; hygroscopic; refractive index 1.784; density 3.464 g/cm<sup>3</sup>; melts at 550°C; vaporizes at 1,265°C; highly soluble in water (145g/100g at 4°C), much greater solubility in hot water (254g/100g at 90°C); soluble in methanol, ethanol and ether; slightly soluble in pyridine; vapor pressure of aqueous solutions at 52 and 68% concentrations at 25°C are 5 and 0.7 torr, respectively.

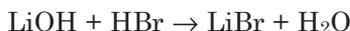
### Thermochemical Properties

$\Delta H_f^\circ$ (LiBr)	-83.94 kcal/mol
$\Delta H_f^\circ$ (LiBr·H <sub>2</sub> O)	-158.36 kcal/mol
$\Delta H_f^\circ$ (LiBr·2H <sub>2</sub> O)	-230.10 kcal/mol
$\Delta H_f^\circ$ (LiBr)(aq)	-95.61 kcal/mol
$\Delta G_f^\circ$ (LiBr)	-81.74 kcal/mol
$\Delta G_f^\circ$ (LiBr·H <sub>2</sub> O)	-142.05 kcal/mol
$\Delta G_f^\circ$ (LiBr·2H <sub>2</sub> O)	-200.90 kcal/mol
$\Delta G_f^\circ$ (LiBr)(aq)	-94.95 kcal/mol
S° (LiBr)	17.75 cal/degree mol
S° (LiBr·H <sub>2</sub> O)	26.2 cal/degree mol

$S^\circ (\text{LiBr} \cdot 2\text{H}_2\text{O})$	38.8 cal/degree mol
$S^\circ (\text{LiBr})(\text{aq})$	22.9 cal/degree mol
$C_p (\text{LiBr})(\text{aq})$	-17.5 cal/degree mol

### Preparation

Lithium bromide is prepared by neutralizing lithium hydroxide or lithium carbonate with an aqueous solution of hydrobromic acid, followed by concentration and crystallization:



The salt is usually obtained as hydrates. Anhydrous lithium bromide is obtained by heating hydrated salt under vacuum.

### Analysis

Elemental composition (Anhydrous LiBr): Li 7.98%, Br 92.02%. The water of crystallization in hydrated salt can be measured by gravimetry. Lithium and bromide ions may be analyzed in diluted aqueous solutions of the salt by AA or ICP spectroscopy and ion chromatography, respectively.

## LITHIUM CARBONATE

[554-13-2]

Formula:  $\text{Li}_2\text{CO}_3$ ; MW 73.89

### Uses

Lithium carbonate is used in enamels, specialty glasses and special ceramic wares. It is used to produce glazes on ceramics and porcelains. It also is used as an additive to molten aluminum fluoride electrolyte in Hall-Heroult process. It is the starting material to prepare many other lithium salts. The compound also is used in medicine as an antidepressant.

### Physical Properties

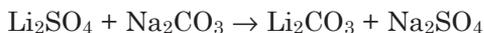
White monoclinic crystals; refractive index 1.428; density 2.11 g/cm<sup>3</sup>; melts at 723°C; decomposes at 1,310°C; low solubility in water (1.54 g/100g) at 0°C; 1.32 g/100g at 20°C), solubility decrease with temperature (0.72g/100g at 100°C); insoluble in acetone and ethanol.

### Thermochemical Properties

$\Delta H_f^\circ$	-290.60 kcal/mol
$\Delta G_f^\circ$	-270.58 kcal/mol
$S^\circ$	21.60 cal/degree mol
$C_p$	23.69 cal/degree mol

**Preparation**

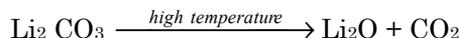
Lithium carbonate is obtained as an intermediate product in recovery of lithium metal from its ore, spodumene (See Lithium). It is prepared by mixing a hot and concentrated solution of sodium carbonate with lithium chloride or sulfate solution.

**Reactions**

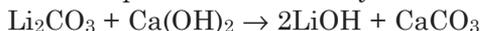
Lithium carbonate reacts with dilute acids, liberating carbon dioxide:



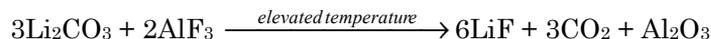
Thermal decomposition yields lithium oxide and carbon dioxide:



Reaction with lime produces lithium hydroxide:



The carbonate reacts with molten aluminum fluoride converting to lithium fluoride:



It combines with carbon dioxide in aqueous slurry forming soluble bicarbonate, which decomposes to carbonate upon heating:



The bicarbonate can not be separated in solid form. It exists only in solution when carbonate dissolves in water saturated with  $\text{CO}_2$  under pressure.

**Analysis**

Elemental composition: Li 18.78%, C 16.25%, O 64.96%. It evolves  $\text{CO}_2$  with effervescence when treated with dilute acids, which turns limewater milky. Lithium may be analyzed in an aqueous solution by atomic absorption or emission spectroscopy and carbonate anion may be determined by ion chromatography.

**LITHIUM CHLORIDE**

[7447-41-8]

Formula:  $\text{LiCl}$ ; MW 42.39

## Uses

Lithium chloride is used in the production of lithium metal by electrolysis. It also is used in metallurgy as a eutectic melting composition with potassium chloride (LiCl 41 mol%: KCl 59 mol%). Other applications are in low temperature dry-cell batteries; as a dehumidifier in air conditioning; in welding and soldering flux; as a desiccant; in fireworks; and in mineral waters and soft drinks.

## Physical Properties

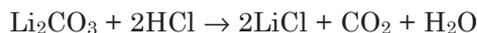
White cubic crystals; granules or powder; hygroscopic; sharp salt-like taste; refractive index 1.662; density 2.068 g/cm<sup>3</sup>; melts at 605°C; vaporizes around 1,360°C; readily dissolves in water (64g/100mL at 0°C); also highly soluble in alcohol and pyridine; moderately soluble in acetone (4.1 g/100mL at 25°C).

## Thermochemical Properties

$\Delta H_f^\circ$ (LiCl)	-97.66 kcal/mol
$\Delta H_f^\circ$ (LiCl·H <sub>2</sub> O)	-170.3 kcal/mol
$\Delta H_f^\circ$ (LiCl·2H <sub>2</sub> O)	-242.0 kcal/mol
$\Delta H_f^\circ$ (LiCl·3H <sub>2</sub> O)	-313.4 kcal/mol
$\Delta G_f^\circ$ (LiCl)	-91.87 kcal/mol
$\Delta G_f^\circ$ (LiCl·H <sub>2</sub> O)	-151.0 kcal/mol
S° (LiCl)	14.18 cal/degree mol
S° (LiBr·H <sub>2</sub> O)	24.58 cal/degree mol
C <sub>p</sub> (LiCl)	11.47 cal/degree mol

## Preparation

Lithium chloride may be prepared by reaction of lithium carbonate or lithium hydroxide with hydrochloric acid followed by crystallization:



Crystallization above 95°C yields anhydrous salt. Hot solution upon cooling forms crystals of monohydrate, LiCl·H<sub>2</sub>O.

Lithium chloride can be synthesized from its elements by heating lithium metal with chlorine gas. It also may be obtained from natural brine.

## Analysis

Elemental composition: Li 16.37%, Cl 83.63%. The aqueous solution of the salt may be analyzed for lithium metal by AA or ICP (See Lithium) and for chloride by titration against a standard solution of silver nitrate or mercury nitrate, or by ion chromatography.

## LITHIUM FLUORIDE

[7789-24-4]

Formula: LiF; MW 25.94

**Uses**

The important uses of lithium fluoride are as flux in glasses, vitreous enamels and glazes; in soldering and welding aluminum; and its prisms in infrared spectrophotometers. The compound also is used for storing solar energy.

**Physical Properties**

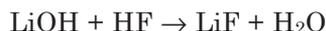
White cubic crystals; refractive index 1.3915; density 2.635 g/cm<sup>3</sup>; melts at 845°C; vaporizes at 1,676°C; very slightly soluble in water 0.27 g/100g at 18°C; soluble in hydrofluoric acid; insoluble in alcohol.

**Thermochemical Properties**

$\Delta H_f^\circ$	-147.22 kcal/mol
$\Delta G_f^\circ$	-140.47 kcal/mol
$S^\circ$	8.52 cal/degree mol
$C_p$	9.94 cal/degree mol

**Preparation**

Lithium fluoride is prepared by treating an aqueous solution of lithium hydroxide or lithium carbonate with aqueous hydrofluoric acid:

**Analysis**

Elemental composition: Li 26.75%, F 73.25%. An aqueous solution prepared by dissolving 100 mg in a liter of water may be analyzed for lithium by AA or ICP spectrophotometry and for fluoride by ion chromatography or by using a fluoride ion selective electrode.

## LITHIUM HYDRIDE

[7580-67-8]

Formula: LiH; MW 7.949

**Uses**

Lithium hydride is used as a reducing and condensation agent in organic reactions. It converts acid chlorides to aldehydes. It also is used in several other organic syntheses; and to prepare lithium aluminum hydride. Lithium hydride also is used as a portable source of hydrogen; and for preparing many lithium salts. It also is used for storing thermal energy for space power stations.

**Physical Properties**

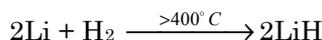
White crystalline solid; cubic crystals; density 0.82 g/cm<sup>3</sup>; melts at 686.4°C; decomposes in water; soluble in acids.

**Thermochemical Properties**

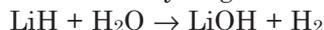
$\Delta H_f^\circ$	-21.64 kcal/mol
$\Delta G_f^\circ$	-16.34 kcal/mol
$S^\circ$	4.783 cal/degree mol
$C_p$	6.66 cal/degree mol

**Preparation**

Lithium hydride is prepared by heating lithium metal with hydrogen above 440°C. The reaction is exothermic and can be controlled once it is initiated, without external heating. The heat of formation is greater than that of sodium hydride:

**Reactions**

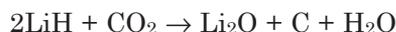
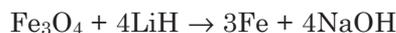
Lithium hydride reacts vigorously with water, forming lithium hydroxide with the evolution of hydrogen:



The hydride also reacts with ammonia forming lithium amide and evolving hydrogen:

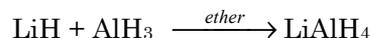


Lithium hydride is a strong reducing agent and would, therefore, react with compounds that contain oxygen. Even many highly stable oxides of metals and nonmetals can be reduced. It reduces metal oxides to metals and carbon dioxide to carbon:



It undergoes violent reactions with oxidizing agents.

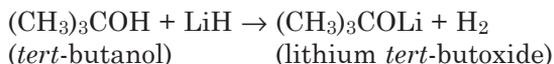
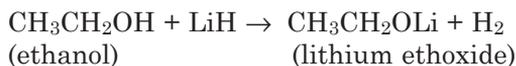
Lithium hydride reacts with aluminum hydride forming lithium aluminum hydride, a powerful reducing agent:



Lithium hydride consisting of Li<sup>+</sup> and H<sup>-</sup> ions exhibits properties of an ionic salt, both cationic and anionic; such as a strong electrolyte. Thus, when electrolyzed at temperatures slightly below its melting point, it dissociates to Li<sup>+</sup>

and  $H^-$  ions. Hydrogen gas is liberated at the anode.

The hydride ion,  $H^-$  being a strong base, would react with alcohols, forming alkoxides and liberating hydrogen:



## LITHIUM HYDROXIDE

[1310-65-2]

Formula: LiOH; MW 23.95

Synonym: lithium hydrate

### Uses

Lithium hydroxide is used as an electrolyte in certain alkaline storage batteries; and in the production of lithium soaps. Other uses of this compound include its catalytic applications in esterification reactions in the production of alkyd resins; in photographic developer solutions; and as a starting material to prepare other lithium salts.

### Physical Properties

White tetragonal crystals; refractive index 1.464; density 1.46 g/cm<sup>3</sup>; melts at 450°C; decomposes at 924°C; dissolves in water (12.8g/100g at 20°C and 17.5 g/100g at 100°C); slightly soluble in alcohol.

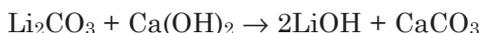
The monohydrate is white monoclinic crystalline solid; refractive index 1.460; density 1.51 g/cm<sup>3</sup>; soluble in water, more soluble than the anhydrous salt (22.3g and 26.8g/100g at 10 and 100°C, respectively); slightly soluble in alcohol; insoluble in ether.

### Thermochemical Properties

$\Delta H_f^\circ$	-115.90 kcal/mol
$\Delta G_f^\circ$	-104.92 kcal/mol
$S^\circ$	10.23 cal/degree mol
$C_p$	11.87 cal/degree mol

### Preparation

Lithium hydroxide is prepared by the reaction of lithium carbonate with calcium hydroxide:



Calcium carbonate is filtered out and the solution is evaporated and crystallized. The product obtained is the monohydrate,  $LiOH \cdot H_2O$ . The anhy-

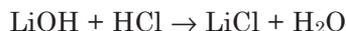
drous compound is obtained by heating the hydrate above 100°C in vacuum or carbon dioxide-free air.

The hydroxide also may be prepared by treating lithium oxide with water.

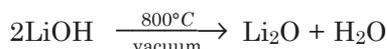
### Reactions

Lithium hydroxide is a base. However, it is less basic than sodium or potassium hydroxide.

The compound undergoes neutralization reactions with acids:



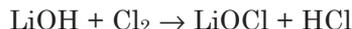
Heating the compound above 800°C in vacuum yields lithium oxide:



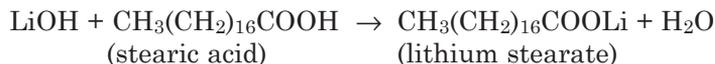
Lithium hydroxide readily absorbs carbon dioxide, forming lithium carbonate:



Passing chlorine through a solution of lithium hydroxide yields lithium hypochlorite:



Saponification of fatty acids with lithium hydroxide produces lithium soaps.



### Analysis

Elemental composition: Li 28.98%, H 4.21%, O 66.80%. An aqueous solution of the compound may be analyzed for lithium by various methods (See Lithium). The basicity of the solution can be measured by acid-base titration using a standard solution of HCl and either a color indicator or a pH meter.

## LITHIUM IODIDE

[10377-51-2]

Formula: LiI; MW 133.85

The monohydrate, LiI·H<sub>2</sub>O [17023-24-4]; dihydrate, LiI·2H<sub>2</sub>O [17023-25-5]; and the trihydrate, LiI·3H<sub>2</sub>O [7790-22-9] are also known.

**Uses**

Lithium iodide is used in photography; and its aqueous solution as an absorbent in refrigeration.

**Physical Properties**

White cubic crystals; refractive index 1.955; density 4.076 g/cm<sup>3</sup>; melts at 449°C; vaporizes around 1,180°C; highly soluble in water (165 g/100g at 20°C), solubility greatly increases in hot water (433g/100g at 80°C); also very soluble in methanol (343 g/100g at 20°C) and ammonia; soluble in acetone (42.6g/100g at 18°C).

The trihydrate, LiI · 3H<sub>2</sub>O, is a yellowish solid (due to the release of iodine when exposed to air); hexagonal crystals; hygroscopic; density 3.48 g/cm<sup>3</sup>; loses iodine when heated in air; loses one molecule of water of crystallization at 73°C becoming dihydrate, LiI · 2H<sub>2</sub>O and loses the second molecule at 80°C, forming monohydrate, LiI · H<sub>2</sub>O and becomes anhydrous at 130°C; highly soluble in water; soluble in ethanol and acetone.

**Thermochemical Properties**

$\Delta H_f^\circ$ (LiI)	-64.63 kcal/mol
$\Delta H_f^\circ$ (LiI · H <sub>2</sub> O)	-141.09 kcal/mol
$\Delta H_f^\circ$ (LiI · 2H <sub>2</sub> O)	-212.81 kcal/mol
$\Delta H_f^\circ$ (LiI · 3H <sub>2</sub> O)	-284.93 kcal/mol
$\Delta H_f^\circ$ (LiI)(aq)	-79.75 kcal/mol
$\Delta G_f^\circ$ (LiI)	-64.60 kcal/mol
$\Delta G_f^\circ$ (LiI · H <sub>2</sub> O)	-127.00 kcal/mol
$\Delta G_f^\circ$ (LiI · 2H <sub>2</sub> O)	-186.50 kcal/mol
$\Delta G_f^\circ$ (LiI)(aq)	-82.40 kcal/mol
S° (LiI)	20.74 cal/degree mol
S° (LiI · H <sub>2</sub> O)	29.40 cal/degree mol
S° (LiI · 2H <sub>2</sub> O)	44.0 cal/degree mol
S° (LiI)(aq)	29.80 cal/degree mol
C <sub>p</sub> (LiI)	-12.20 cal/degree mol
C <sub>p</sub> (LiI)(aq)	-17.60 cal/degree mol

**Preparation**

The trihydrate salt is obtained by neutralization of lithium hydroxide or lithium carbonate solution with pure hydriodic acid followed by concentration of the solution for crystallization:



When heated in a vacuum, the trihydrate dehydrates to anhydrous salt.

**Analysis**

Elemental composition (anhydrous LiI): Li 5.18%, I 94.82%. The water of crystallization may be measured by gravimetry. An aqueous solution may be appropriately diluted and analyzed for lithium by AA or ICP spectrophotom-

etry (See Lithium) and for the iodide ion by ion chromatography. Iodide may be alternatively analyzed by the leuco crystal violet method. Upon addition of potassium peroxymonosulfate,  $\text{KHSO}_5$ , iodide is selectively oxidized to iodine, which instantaneously reacts with the colorless indicator reagent known as leuco crystal violet [4,4',4''-methylidynetris(N,N-dimethylaniline)] to produce a violet colored dye. Absorbance or transmittance of the solution measured at 592nm by a spectrophotometer or a filter photometer is proportional to concentration of iodide in solution (APHA, AWWA and WEF. 1998. *Standard Methods for the Examination of Water and Wastewater*, 20<sup>th</sup> ed. Washington, D.C.: American Public Health Association.)

## LITHIUM NITRATE

[7790-69-4]

Formula:  $\text{LiNO}_3$ ; MW 68.946

Forms a stable trihydrate,  $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$

### Uses

Lithium nitrate is used in fireworks to impart carmine-red color to the flame. Its mixtures with other alkali nitrates produce very low melting eutectics, which are used as heat-transfer media.

### Physical Properties

White trigonal crystals; hygroscopic; refractive index 1.735; density 2.38  $\text{g/cm}^3$ ; melts to a clear melt at 264°C; decomposes at 600°C; highly soluble in water (90g/100g at 28°C; solubility greatly increases with temperature (234g/100g at 100°C); also, soluble in methanol, pyridine and ammonia solution.

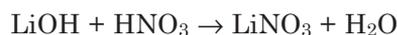
The trihydrate,  $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$ , consists of colorless needles; loses water of crystallization on strong heating; soluble in water, methanol and acetone.

### Thermochemical Properties

$\Delta H_f^\circ$	( $\text{LiNO}_3$ )	-147.47 kcal/mol
$\Delta H_f^\circ$	( $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$ )	-328.5 kcal/mol
$\Delta G_f^\circ$	( $\text{LiNO}_3$ )	-91.1 kcal/mol
$\Delta G_f^\circ$	( $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$ )	-263.8 kcal/mol
$S^\circ$	( $\text{LiNO}_3$ )	21.5 cal/degree mol
$S^\circ$	( $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$ )	53.4 cal/degree mol

### Preparation

Lithium nitrate is prepared by neutralization of lithium hydroxide or lithium carbonate with nitric acid followed by evaporation of the solution and strong heating at 200°C in vacuum to yield the anhydrous salt:



**Analysis**

Elemental composition (anhydrous salt): Li 10.07%, N 20.32%, O 69.62%. A diluted aqueous solution may be analyzed for lithium by AA or ICP method (See Lithium) and nitrate ion by either ion-specific electrode or by ion chromatography.

**LITHIUM NITRIDE**

[26134-62-3]

Formula:  $\text{Li}_3\text{N}$ ; MW 34.83

**Uses**

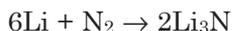
Lithium nitride is used as a catalyst to prepare boron nitride. It also is used as a reducing and nucleophilic reagent in organic synthesis, and to convert metals into their nitrides.

**Physical Properties**

Red hexagonal crystals or free-flowing fine red powder; density 1.27 g/cm<sup>3</sup>; melts at 813°C; an excellent solid ionic conductor; conductivity  $4 \times 10^{-2}$  mho/cm at 227°C; decomposes in water.

**Preparation**

Lithium nitride is prepared by passing dry nitrogen gas over lithium metal:



The reaction is exothermic and occurs at ordinary temperatures. The reaction may be controlled by adjusting temperature and nitrogen flow rate. The reaction proceeds rapidly when the metal is heated in nitrogen.

**Reactions**

Lithium nitride is a strong reducing agent. Thus, all its reactions involve reduction. It ignites in air and reacts with water to form lithium hydroxide and ammonia:



Lithium nitride reduces metal oxides and many metal chlorides to metallic state. It reduces copper(I) chloride to copper. Most of these reactions are exothermic.

**Hazard**

Lithium nitride ignites in air. Violent decomposition can occur when mixed with oxidizing agents.