

C-Li (Carbon-Lithium) System

James Sangster

Equilibrium Diagram

The assessed C-Li phase diagram is shown in Fig. 1.

Information concerning this system was reviewed by [Shunk], [Elliott], and [1989Oka]. The principal features of this diagram are: (a) a liquid (liquidus incompletely defined), (b) eutectic temperature and composition, and (c) the compound C_2Li_2 . [1957Fed] performed thermal analysis on mixtures of 50-99.5 at.% Li, and measured the vapor pressure of compositions 86, 89, and 92 at.% Li. [1957Fed] also reported temperature arrests at approximately 560, 440, and 410 °C. These were attributed [1957Fed] to solid-solid transitions of C_2Li_2 . As discussed below, the evidence for such transformations in solid C_2Li_2 is not definitive, and these have been omitted from the equilibrium diagram. (All data points of [1957Fed] were tabulated in [1989Oka].)

The equilibrium phases in this system were established by [1962Sec1, 1962Sec2, 1967Sec]. These authors equilibrated mixtures of 2-55 at.% Li and quenched samples from 350 to 1000 °C. XRD showed that C_2Li_2 is the only compound that is in equilibrium with C and Li. Chemical analysis was performed by flame photometry and also by combustion followed by absorption in alkaline solution.

[1957Fed] observed eutectic arrests as far as 99.5 at.% Li. The reported eutectic [1957Fed] is 165 °C at >99 at.% Li; the experimental M.P. of Li is 176 °C. In [1981Shi] it is stated that "...carbon is not soluble in lithium below 650 °C." This qualitative statement was unsupported by any mention of measurement or data source. The freezing point depression relation (or law of limiting slopes) at the Li extreme is

$$(dX_{\text{liquid}}/dT) - (dX_{\text{solid}}/dT) = \Delta_{\text{fus}}H/RT_{\text{fus}}^2, \quad (\text{Eq 1})$$

where the first and second terms on the LHS are the limiting slopes of liquidus and solidus respectively, $\Delta_{\text{fus}}H$ is the enthalpy of fusion of Li and T_{fus} is the M.P. of Li.

Assuming zero solid solubility of C in Li and discrete differentials, Eq. 1 may be rearranged to

$$\Delta X_{\text{liquid}} = (\Delta_{\text{fus}}H)(\Delta T)/RT_{\text{fus}}^2. \quad (\text{Eq 2})$$

The accepted M.P. of Li is 180.6 °C [Melt], while the experimental value is 176 °C.

On the assumption that the experimental eutectic temperature is $180.6 - 176 = 4.6$ °C too low (i.e., $\Delta T = 4.6$ °C) and that the enthalpy of fusion of Li is 3 kJ mol^{-1} [1983Cha], $\Delta X_{\text{liquid}} = 0.008$, in agreement with experiment [1957Fed].

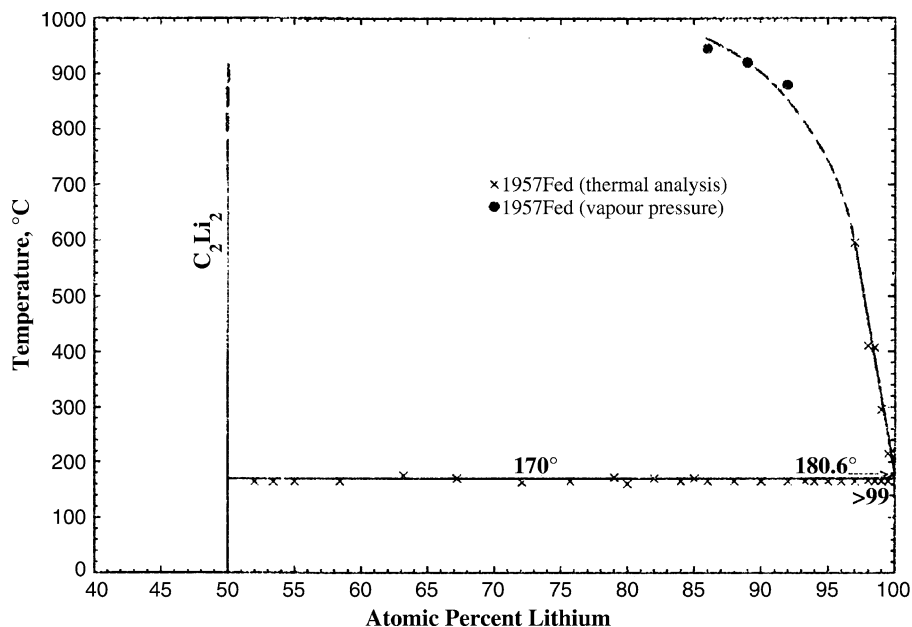


Fig. 1 Assessed C-Li phase diagram

Section II: Phase Diagram Evaluations

Compounds

The alkali metals exhibit three types of intermediate compounds with carbon. For lithium, these may be designated as:

- (1) simple C-Li compounds C_xLi_y
- (2) lithium-graphite intercalation compounds
- (3) lithium-fullerene exohedral and endohedral compounds

In the chemical literature, molecular formulas for C-Li compounds have been written with either C or Li placed first, without much consistency. In the present instance, C will always come before Li.

Simple C-Li Compounds C_xLi_y

C_2Li_2 (lithium acetylide, lithium carbide) was prepared by heating lithium and carbon in vacuo at temperatures between 525 and 1000 °C [1898Gun, 1955Her, 1965Juz1, 1967Juz, 1967Sec]. The carbon may be in the form of diamond, graphite, or amorphous carbon. C_2Li_2 was found in the products of the reaction in vacuo between Li vapor and C_3 - C_4 alkenes, $CHCl_3$ or CCl_4 [1975Mor, 1983Lan]. It was identified by its reaction product with water or D_2O [1898Gun, 1975Mor, 1983Lan]. It was characterized by XRD [1962Sec1, 1962Sec2, 1962Sec3, 1965Juz1, 1967Sec, 1967Juz].

C_2Li_2 probably decomposes before melting [1967Mes]. [1955Her] prepared the compound at 1000 °C without mentioning melting or decomposition. Knudsen effusion experiments (decomposition products) were performed at 700-1300 °C [1989Kud, 1992Kud, 1993Kud]. A “melting

point” of 927 °C is given in a recent compilation [1999Bin] without data source or explanation.

There is evidence that C_2Li_2 may exist in more than one crystalline form. This is discussed under “Crystal Structures and Lattice Parameters” below.

Recently a number of simple C-Li compounds (other than C_2Li_2) have been prepared. They are listed in Table 1, together with reaction conditions and identification methods. They may be considered perlithiated versions of the corresponding hydrocarbons. All are stable at RT, except C_4Li_4 (stable at -20 °C and decomposing slowly at RT). It should be noted that the existence of most of these compounds was inferred from their reaction products with water or D_2O . Only C_4Li_4 was detected in situ [1978Rau]. None have been isolated and characterized by other means.

Lithium-Graphite Intercalation Compounds

These are also called “lamellar,” “layered,” “interstitial” or “insertion” compounds. All alkali metals form graphite intercalation compounds, but those with Li or Na are fewer and are formed less easily than those of the heavier alkali metals. The structure of graphite and metal intercalation compounds is shown schematically in Fig. 2. Graphite has a layered structure, in which the carbon atoms are arranged in parallel planes, in each of which they form a network of hexagons [1971Nov]. There is no chemical bonding between the layers and so alkali metals can be inserted rather easily between the layers. The separation of the adjacent layers increases somewhat when alkali metal atoms are inserted.

The conventional method of indicating the stoichiometry of metal-graphite intercalation compounds is C_xM , where x

Table 1 Preparation of small C-Li compounds (excluding C_2Li_2)

Compound	Reactants	Solvent	Temperature, °C	Identification Reaction (analytical method)	Reference
C_3Li_4	Propyne, butyllithium	Hexane	Reflux	H_2O (IR)	[1965Wes, 1969Wes]
CLi_4	Li, CCl_4	In vacuo	800-1000	D_2O (MS)	[1972Chu]
C_2Li_6	Li, C_2Cl_6	In vacuo	800-1000	D_2O (MS)	[1972Chu]
C_5Li_4	1,3-pentadiyne, butyllithium, TMEDA	Butane	Reflux	H_2O , D_2O (GLC, MS)	[1973Chw]
C_2Li_4	Li, 1-alkenes	In vacuo	700-800	H_2O , D_2O (NMR, GLC, MS)	[1975Mor]
C_3Li_4					
C_2Li_6					
C_2Li_4	Li, halogenated alkenes	In vacuo	800-1000	D_2O in THF (GLC)	[1975Sne]
C_3Li_4					
C_2Li_6					
C_4Li_4	C_2Li_2 , hv	Liquid NH_3	-45	(a)	[1978Rau]
C_3Li_6	Li, halogenated benzenes	In vacuo	800	D_2O (GLC, MS)	[1978Shi]
C_3Li_4					
CLi_4	Li, $CHCl_3$	In vacuo	750	D_2O (GLC, MS)	[1983Lan]
C_2Li_6	Li, CCl_4	In vacuo	750	D_2O (GLC, MS)	

(a) In situ analysis (NMR, IR, Raman in liquid NH_3 , or DMF)

DMF = dimethyl formamide

GLC = gas-liquid chromatography

IR = infrared spectroscopy MS = mass spectrometry NMR = nuclear magnetic resonance THF = tetrahydro furan Raman = Raman spectroscopy

TMEDA = tetramethyl ethylenediamine

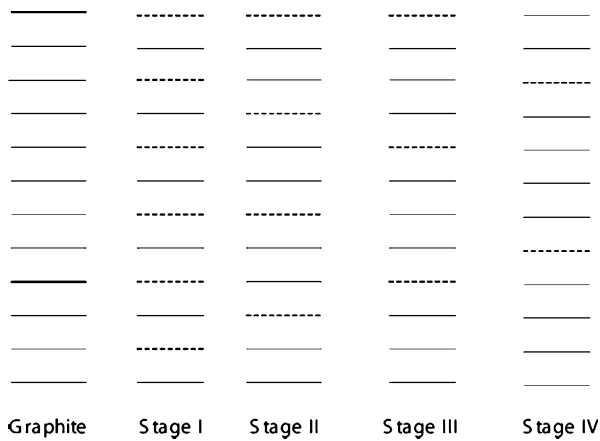


Fig. 2 Schematic representation of the structure of graphite and lithium-graphite intercalation compounds. *Solid lines*: graphite layers. *Dashed lines*: metal layers. The patterns repeat themselves in both directions

may be an integer or fractional number. The formula C_xM does not represent a molecule of $(x + 1)$ atoms; rather, it indicates merely the atom ratio C/M in a macroscopic sample.

The intercalation compounds (Fig. 2) are named “first stage,” “second stage,” etc. according to the number of graphite layers separating the metal layers. The stoichiometry C_xM assigned to a particular stage compound should be regarded as nominal or average. The overall stoichiometry is established by chemical reaction and analysis, the particular stage by XRD.

The common methods for the preparation of Li-graphite intercalation compounds are:

- reaction with Li vapor
- reaction with liquid Li
- in organic solvent solution

A summary is given in Table 2. Both natural and synthetic graphite have been used.

In general, the temperature must be kept below 500 °C in order to suppress formation of C_2Li_2 . In the preparation in solution, the compound precipitates from solution and is isolated for characterization. In addition to those mentioned in Table 2, [1991Dah] used an electrochemical method at 0-70 °C. The compounds C_6Li_x ($0 < x < 1$) were identified by an amperometric titration procedure and in situ XRD.

The direct combination of graphite and Li may be effected at high pressure. The method is reviewed in [1994Con]. Representative data are given in Table 3. The reaction is usually carried out under Ar. [1979Bil1] and [1979Bil2] used a Li-Na mixture; no Na entered the graphite because its affinity for graphite is lower than that of Li [1977Her], and the two alkali metals form neither intermediate compounds nor solid solutions [1990Mas]. Annealing in vacuo or under low pressure Ar was sometimes used to obtain large samples of C_6Li [1972Gue, 1975Gue]. C_6Li prepared at low or high pressure is stable at ambient pressure. Compounds C_xLi ($x < 6$) decompose slowly at ambient pressure [1989Bel, 1989Sya, 1994Udo] or are stable under these conditions [1992Nal].

From Tables 2 and 3 and an examination of the pertinent literature, it may be concluded that first stage C_6Li is the principal lithium-graphite intercalation compound, and it

Table 2 Preparation of lithium-graphite intercalation compounds by various methods (low pressure)

Compound Reported	Stage	Reactant	Solvent	Temperature, °C	Reference
C_4Li (?)	...	Li vapor	...	500	[1955Her]
C_6Li	1	Li vapor	[1965Juz2]
$C_{12}Li$	2	Li vapor	
$C_{18}Li$	3Li vapor	
C_6Li	1	Li vapor	[1966Bag]
$C_{18}Li$	2 Li vapor	
$C_{36}Li$	4	Li vapor	
$C_{72}Li$	8	Li vapor	
C_6Li	1	Li liquid	...	400	[1968Sal]
$C_{41.5\pm 1.5}Li$...	Li-naphthalene	THF	Ambient	[1965Ste]
$C_{17.5\pm 1.5}Li$...	Li-naphthalene	THF	Ambient	
$C_{16}Li$...	Li-naphthalene	THF	Ambient	[1965Gol]
$C_{40}Li$...	Li-diphenyl	THF	Ambient	
...	2,3	Li-phenanthrene	Ethers	...	[1996Miz, 1997Miz]
C_6Li	1	Li vapor	...	< 400	[1975Gue]
$C_{15.7\pm 0.4}Li$	2	Li vapor	...	< 400	
$C_{23.7\pm 1.5}Li$	2	Li vapor	...	< 400	
$C_{19.33}Li$	3	Li vapor	...	< 400	
$C_{37}Li$	4	Li vapor	...	< 400	

THF = tetrahydro furan

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Table 3 Preparation of lithium-graphite intercalation compounds at elevated pressure

Compound Reported	Stage	Temperature, °C	Pressure	Reference
C ₆ Li	1	Ambient	...	[1972Gue]
C ₆ Li	1	Ambient	10-20 kbar	[1975Gue]
C ₁₂ Li	1 and/or 2	Ambient	10-20 kbar	
C ₁₈ Li	2 and/or 3	Ambient	10-20 kbar	
C ₂₇ Li	3 and/or 4	Ambient	10-20 kbar	
C ₆ Li	1	150	...	[1979Bil1] (a)
C ₆ Li	1	150	...	[1979Bil2] (a)
C ₁₂ Li	2	150	...	
...	3	150	...	
C ₆ Li	1	<350	60 kbar	[1982Avd, 1982Mor]
C ₆ Li	1	200-300	2.8 Gpa	[1983Sem]
C _{2-2.5} Li	1	1		
C ₆ Li	1	350	30-40 kbar	[1989Bel]
C ₃ Li	1	350	30-40 kbar	
C ₂ Li	1	350	30-40 kbar	
C ₆ Li	1	<180	<3 kbar	[1989Sya]

(a) Reactant was Li-Na mixture

may be prepared at both low and high pressures. The stoichiometry of higher-stage compounds is variable [1975Gue]. This is so because, in low-pressure preparative methods, the stoichiometry is sensitive to the temperature (i.e., the vapor pressure of Li) and in high-pressure methods, it is sensitive to the pressure [1984Sem]. Although these intercalation compounds are not part of the overall C-Li phase diagram (Fig. 1), an “equilibrium phase diagram” of intercalated compounds by themselves may be constructed [1991Dah]. According to [1991Dah], intercalation compounds of stage greater than 4 are not (thermodynamically) stable.

Lithium-Fullerene Compounds

The fullerenes are closed carbon-cage molecules containing only pentagonal and hexagonal rings. They have the general formula C_n, where *n* is an even integer greater than 20 [1995Fow]. The best-known fullerenes are C₆₀ (“soccer ball” shape) and C₇₀.

C₆₀ may be prepared in an arc between graphite electrodes in subatmospheric Ar or He. The C₆₀ is extracted from the smoke of carbon particles by an organic solvent [1990Hau, 1990Kra, 1990Tay, 1991Bet]. It may also be prepared by a vaporizing laser beam falling on a graphite surface under a high-pressure stream of He [1985Kro] or in a static low-pressure Ar atmosphere [1990Mei].

All the alkali metals form *exohedral* and *endohedral* compounds with fullerene. In exohedral lithium compounds, the Li atoms and fullerene molecules occupy sites on a crystalline lattice; in endohedral compounds, the Li atoms are inside the fullerene cages [1998Lah]. The preparation of exohedral compounds is summarized in Table 4. In the synthesis with LiN₃, the mixtures were heated in vacuo at about 533 K, allowing complete LiN₃ decomposition and insertion of Li into the crystal lattice. The crystallinity was improved by moderate annealing at 550 K [1999Cri].

Table 4 Preparation of exohedral Li-fullerene compounds

Method	<i>x</i> in Li _{<i>x</i>} C ₆₀	Comments	Reference
Electrochemical	0.5, 2,3,4,12	Potentiometric titration Compounds not isolated	[1992Cha]
LiN ₃ + C ₆₀	1	Characterized by XRD	[1999Yas]
LiN ₃ + C ₆₀	12	Characterized by XRD	[1999Cri]
LiN ₃ + C ₆₀	1-6, 8, 10, 12, 16, 20, 24, 28	Characterized by XRD	[2001Yas]

The Li-C₆₀ endohedral compound is conventionally indicated by Li@C₆₀. It is prepared as thin films by in vacuo bombardment of C₆₀ with Li⁺ ions at 15-90 eV [1996Tel]. The pure compound may be isolated by differential solution in organic solvents and/or by chromatography [1998Kra1]. Li@C₇₀ was prepared and isolated in a similar manner [1998Kra2]. From ab initio calculations, it was concluded [1995Tom] that the Li-C₆₀ bond in Li@C₆₀ is partially ionic.

Crystal Structures and Lattice Parameters

These are presented in Tables 5 and 6, respectively.

C₂Li₂ and Perlithiated Carbon Compounds

[1957Fed] observed thermal arrests in the C-Li system between 50 and 100 at.% Li. They also reported unindexed x-ray diffractograms of quenched Li-C₂Li₂ and C-C₂Li₂ mixtures. From the data they concluded that C₂Li₂ shows three transitions at approximately 410, 440, and 560 °C. [1967Sec] followed the same procedure of preparation of C₂Li₂ at high temperature, slow cooling, annealing,

Table 5 C-Li Crystal Structure Data

Phase	Composition at.% Li	Pearson symbol	Space group	Strukturbericht designation	Prototype	Reference
C	0	<i>hP4</i>	<i>P6₃/mmc</i>	<i>A9</i>	C(graphite)	[King1]
C	0	<i>cF8</i>	<i>Fd$\bar{3}m$</i>	<i>A4</i>	C(diamond)	[King1]
C	0	<i>cF240</i>	<i>Fm$\bar{3}m$</i>		C ₆₀	[1991Hei]
C ₇₂ Li	1.4	<i>hP*</i>				[1966Bag]
C ₄₀ Li	2.4	<i>hP*</i>				[1965Gol]
C ₃₆ Li	2.7	<i>hP*</i>				[1966Bag]
C ₁₈ Li	5.3	<i>hP*</i>				[1965Juz2]
C ₁₆ Li	5.9	<i>hP*</i>				[1965Gol]
C ₁₂ Li	7.7	<i>hP*</i>	<i>P6/mmm</i>			[1975Gue]
C ₆ Li	14.3	<i>hP7</i>	<i>P6/mmm</i>			[1975Gue]
C ₂ Li ₂ (a)	50.0	<i>oI8</i>	<i>Immm</i>		Cs ₂ O ₂	[1965Juz1]
C ₂ Li ₂ (a)	50.0	<i>mP78</i>	<i>P2/m</i>			[1962Sec3]
Li	100.0	<i>cI2</i>	<i>Im$\bar{3}m$</i>	<i>A2</i>	W	[King1]

(a) C₂Li₂ may exist in more than one crystal structure. See text

Table 6 C-Li Lattice Parameter Data

Phase	Composition, at.% Li	Lattice parameter, nm			Comment	Reference
		<i>a</i>	<i>b</i>	<i>c</i>		
C (dia)	0	0.54308				[Pearson3]
C (gr)	0	0.24612		0.67090		[King1]
C (C ₆₀)	0	1.411				[1991Ste]
		1.4161				[1992Tan]
		1.417				[1991Hei]
		1.4172				[1992Aga]
C ₇₂ Li	1.4	...		2.705		[1966Bag]
C ₃₆ Li	2.7	...		1.375		[1966Bag]
C ₁₈ Li	5.3	0.428 (a)		1.044 (a)		[1965Juz2]
		0.740		0.705		[1966Bag]
C ₁₂ Li	7.7	0.4288		0.7065		[1975Gue]
		0.4290		0.7029		[1965Juz2]
C ₆ Li	14.3	0.4305		0.3706		[1975Gue]
		0.429		0.737		[1965Juz2]
C ₂ Li ₂	(b) 50.0	0.3655	0.5440	0.4830		[1965Juz1]
C ₂ Li ₂	(b) 50.0	0.7801	0.8815	1.0865	$\beta = 76.8^\circ$	[1962Sec3]
Li	100.0	0.35093				[King1]

(a) Approximate value [1965Juz2]

(b) See note (a) of Table 5

quenching and x-ray examination. Only one form of C₂Li₂ was detected [1962Sec1, 1962Sec2, 1967Sec], viz., that of [1962Sec3]. Examination of a single crystal of C₂Li₂ gave the same result [1967Sec]. [1967Juz] observed no change in crystal structure up to 350 °C. [1967Sec] speculated that the evidence of apparently different modifications was an impurity effect.

[1965Juz1] and [1967Juz] found C₂Li₂ to be orthorhombic, whereas [1962Sec3] reported a monoclinic structure. It is to be noted that [1962Sec3] explicitly stated the cooling regimen of the sample prepared at high temperature, but [1965Juz1, 1967Juz] did not. The question as to the

existence of more than one crystalline structure remains open.

Although acetylene is a linear molecule, C₂Li₂ is planar and there is little or no C-Li covalent bonding [1967Mes, 1976Ape, 1985Chi]. The same is true for other perlithiated C-Li molecules, based on IR spectroscopy and ab initio molecular orbital calculations: C₃Li₄, from propyne [1969Wes, 1977Jem, 1996Mar1], C₂Li₆ from ethane [1994Iva], C₅Li₄ from 1,3-pentadiyne [1973Chw], and C₄Li₄ from tetrahydrene [1978Rau].

Lithium-Graphite Intercalation Compounds

The crystal structure of the intercalated compounds is, like graphite itself, primitive hexagonal. [1965Juz2] assigns a space group D_{6h}¹ to C₆Li. The lattice parameters of C₆Li and C₁₈Li of [1966Bag] and [1965Juz2] differ significantly. There may be two different types or the same structure was indexed differently. It is to be noted that the report of [1965Juz2] is essentially an abstract, with no experimental details or discussion, whereas [1975Gue] provides a much fuller account.

Lithium-Fullerene Compounds

The molecular structure of fullerene C₆₀ was suggested by [1985Kro, 1987Kro, 1990Kra] to resemble closely that of a soccer ball. Ab initio calculations [1988Sch] indicated that a cluster of C atoms having 60 vertices and 32 faces (20 hexagonal and 12 pentagonal) would be energetically favored. This structure, a truncated icosahedron, would have I_h overall symmetry, i.e., all the C atoms are equivalent. This assignment was confirmed by NMR measurements [1990Joh, 1991Yan] and Raman/IR spectra [1991Bet].

The arrangement of the C₆₀ molecules in the crystal structure was deduced from powder XRD [1990Kra, 1991Hei]. Originally it was thought that the spheres were stacked in a hexagonal close-packed lattice, with

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$a = 1.002$ nm and $c = 1.636$ nm [1990Kra]. Later more careful examination showed that the crystal structure is fcc [1991Hei] at ambient temperature.

At -24 °C the structure becomes simple cubic (cP240) and $a = 1.404$ nm at 11 K [1991Hei].

According to [1992Jin], this transition probably represents a crystal/plastic crystal transformation. The plausibility of such a first-order transition is supported by ab initio calculations [1991Guo].

The 1:1 compound $C_{60}Li$ is fcc with I_h symmetry, $a = 1.418$ nm [1999Yas]. The lattice parameters of $C_{60}Li_{12}$ were measured in the temperature range 100-533 K [1999Cri]. At 298 K, the crystal is tetragonal, $a = 1.399$ nm, $c = 1.421$ nm; with increasing temperature, these converge to $a = 1.978$ nm at 553 K, indicating an $Fm\bar{3}m$, fcc structure [1999Cri] (the lattice parameters were given only as points on a graph). A series of compounds $C_{60}Li_x$ ($x = 1-28$) was examined by x-ray powder diffraction. The lithium-rich and lithium-poor compounds in this series were fcc; the intermediate compounds displayed a mixture of fcc and tetragonal two-dimensional polymer phases (see "Pressure" section).

Endohedral compounds have been prepared only as thin films, and no crystalline structure data are available. Since the Li atoms are inside the C_{60} cages, it is expected that the crystalline structure of $Li@C_{60}$, for example, would be very similar to C_{60} itself.

Thermodynamics

A short summary of the thermodynamic properties of C_2Li_2 was given by [1976Smi]. Original measurements of the enthalpy of formation are summarized in Table 7. The heat of reaction of C_2Li_2 with water was measured calorimetrically at 17 °C by [1898Gun], who reported a value of -47.3 kJ mol⁻¹ (from diamond). This value was converted to the standard quantity with the use of the enthalpy of formation of diamond [1989Bar] and is shown in Table 7. The value adopted in recent compilations [1982Wag, 1985Cha, 1999Bin] is -59.4 kJ mol⁻¹.

Table 7 Standard enthalpy of formation of C_2Li_2

Method	$\Delta_f H^\circ$ (C_2Li_2 , cr, 298.15 K) kJ mol ⁻¹	Reference
Calorimetry	-43.5	[1898Gun]
Calorimetry	-59.4	[1993Kud] (a)
Knudsen effusion	-68.4	[1993Kud]
Knudsen effusion	-67.7	[1989Kud]
Knudsen effusion	-50.5	[1981Asa]
Vaporization	-65.3	[1977Kat]

(a) The source of this datum given by [1993Kud] is the book *Vapor Pressure of the Chemical Elements* (A. V. Nesmeyanov, Elsevier, Amsterdam, 1963). This is an error, as the book contains no such datum. The probable source is [1960Fur]

The value

$$\Delta_f H^\circ (CLi_4, g, 298.15K) = -239.2 \text{ kJ mol}^{-1}$$

was reported from Knudsen effusion/mass spectrometry by [1993Kud].

An electrochemical cell with graphite cathode and solid-state polyethyleneoxide-LiClO₄ electrolyte [1983Yaz] was used to obtain the following data [1993Yaz] at 60 °C:

$$36C + Li = C_{36}Li; \Delta G = -69.5 \text{ kJ mol}^{-1}$$

$$C_{36}Li + Li = 2C_{18}Li; \Delta G = -48.1 \text{ kJ mol}^{-1}$$

$$0.5C_{18}Li + Li = 1.5C_6Li; \Delta G = -32.2 \text{ kJ mol}^{-1}$$

By means of Hess' Law, one can deduce the formation Gibbs energies

$$18C + Li = C_{18}Li; \Delta G = -58.8 \text{ kJ mol}^{-1}$$

and

$$18C + 3Li = 3C_6Li; \Delta G = -74.9 \text{ kJ mol}^{-1}$$

An electrochemical cell with the LiCl-KCl eutectic as electrolyte at 700 K was used to obtain the formation Gibbs energy [1979Sel]

$$nC(\text{gr}) + 2Li(l) = C_nLi_2; \Delta G = -82.9 \text{ kJ mol}^{-1}$$

where n is indeterminate.

The enthalpy of formation of exohedral lithium fullerenes was calculated by the Born-Haber cycle. For $C_{60}Li_3$, the values are -75 kJ mol⁻¹ [1993Tom] and -59 kJ mol⁻¹. [1996Cla]. For $C_{60}Li_6$, the value is -59 kJ mol⁻¹ [1993Tom].

The same method was used for endohedral $Li@C_{60}$ (-131 kJ mol⁻¹) [1993Wan].

Pressure

The preparation of lithium-graphite intercalation compounds under pressure was described in the section "Compounds."

C_{60} fullerene, like unsaturated organic molecules, can be made to polymerize under certain conditions. Thus at pressures greater than 2 GPa, fullerene polymerizes to form 1-, 2-, or 3-dimensional polymer networks [1994Iwa, 1995Nun, 1996Mar2, 1998Dav, 1999Mar]. Lithium- C_{60} compounds are similarly affected. $C_{60}Li_x$ ($x = 1-28$) compounds under pressure treatment yielded trigonal, tetragonal, or rhombohedral structures [1999Yas, 2001Man, 2001Yas].

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C-Li evaluation contributed by **J. Sangster**, Sangster Research Laboratories, P.O. Box 49562, 5122 Cote des Neiges, Montreal, Quebec, Canada, H3T 2A5. Literature searched through 2004.