

C-Na (Carbon-Sodium) System

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Equilibrium Diagram

There is no phase diagram available for this system. It may be conjectured that it would be similar to that for the C-Li system, and so would show (a) the compound C_2Na_2 , (b) a liquid and (c) a eutectic of composition very close to 100 at.% Na and temperature very close to the M.P. of Na.

Data for the solubility of C in liquid Na have been reported in [1957Gra, 1967Lun, 1969McK, 1970Geh, 1970Lon, 1972Sal, 1973Ack, 1974Ain]. Pertinent experimental details are summarized in Table 1. The data, plotted in Fig. 1, were fitted to the equation:

$$\text{Log}_{10}S = A - B/T \quad (\text{Eq 1})$$

where S is the solubility in mass/ppm and T is in kelvin. Reported values of A and B are given in Table 2; a partial review of experimental results is given in [1982Rum]. In two earlier studies [1957Gra, 1967Lun] the source of carbon in the equilibration process was a graphite rod; it is, however, notoriously difficult to separate the undissolved carbon from the solution by filtering [1970Lon]. This difficulty was circumvented in later work [1969McK, 1970Geh, 1970Lon, 1974Ain] by introducing the carbon through a thickness of Ni metal, which acted as a semi-permeable membrane. The equilibrium concentrations of

Table 1 Solubility of C in liquid Na: summary of experimental conditions

Temperature, °C	Source of carbon	Analytical method	O impurity in Na, wppm	Reference
147-700	Graphite	Chemical oxidation	40 and 266	[1957Gra]
155-455	Graphite	Chemical oxidation	...	[1967Lun]
700-1015	(C in Na)//Ni	Combustion/radiochemical	~18	[1969McK, 1970Geh]
600-950	(C in Na)//Ni or (CO+CO ₂)//Ni	Combustion	10-400	[1970Lon]
575-700	C in Fe	EMF	1-240	[1972Sal]
351-513	C ₂ Na ₂	Reaction with H ₂ O	...	[1973Ack]
490-823	(C in Na)//Ni	Combustion/radiochemical	<450	[1974Ain]

Note: the indication “//Ni” means that Ni foil was used as an “atomic filter,” i.e., the foil was permeable only to single C atoms and not particulate carbon

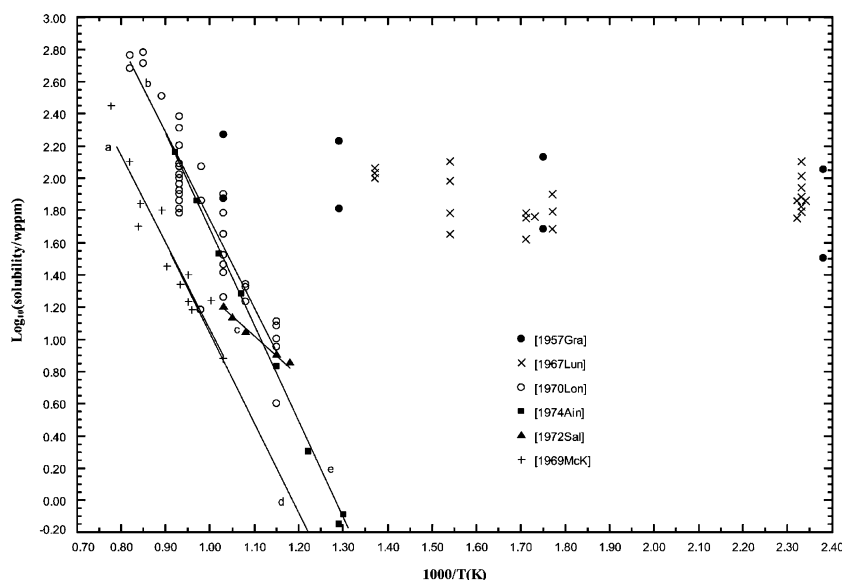


Fig. 1 Solubility of carbon in liquid sodium. In order to avoid clutter, not all data are plotted. Straight lines from (Table 2): a = [1969McK, 1970Geh]; b = [1970Lon]; c = [1972Sal]; d = [1973Joh]; and e = [1974Ain]

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Table 2 Solubility of C in liquid Na: reported values of parameters in the equation $\text{Log}_{10}S = A - B/T$ (Eq 1) (S , mass/ppm; T , K)

A	B	Temperature range, °C	Reference
2.15 (a)	297 (a)	147-700	[1957Gra]
2.44 (b)	163 (b)	147-700	[1957Gra]
6.50	5450	700-1015	[1969McK, 1970Geh]
7.20	5465	600-950	[1970Lon]
3.70	2440	575-700	[1972Sal]
6.71	5679	273-827	[1973Joh]
7.646	5970	490-832	[1974Ain]
7.02	5642	400-985	[1982Rum]

(a) 40 ppm oxygen, (b) 266 ppm oxygen

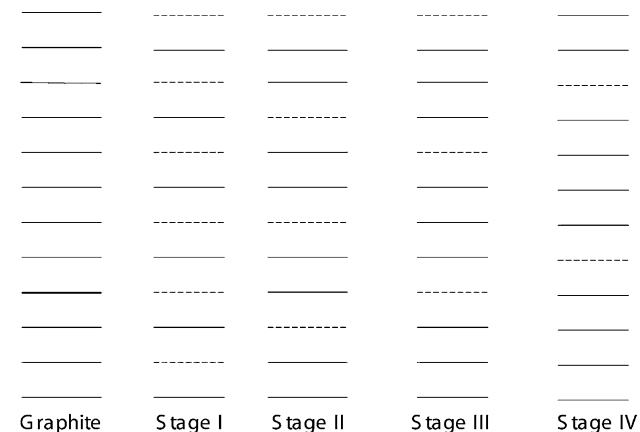


Fig. 2 Schematic representation of the structure of graphite and sodium-graphite intercalation compounds. *Solid lines*: graphite layers. *Dashed lines*: metal layers. The patterns repeat themselves in both directions

carbon found this way were extrapolated to unit carbon activity. In other determinations, the carbon was introduced as Na_2C_2 [1973Ack] or from a solution in iron [1972Sal].

The Na_2C_2 solubility data [1973Ack] were converted to unit carbon activity by a thermodynamic calculation using experimentally determined Gibbs energies of formation of Na_2C_2 [1973Joh]. The solubility measurements [1973Ack] were done in the range 351-513 °C; the solubility parameters [1973Joh] in Table 2 were based on the assumption that the C_2Na_2 solubilities were extrapolatable to 1100 K.

From Fig. 1 it is evident that the earlier results [1957Gra, 1967Lun] are erroneous. The remaining data [1970Lon, 1972Sal, 1974Ain] may be represented by Eq 1 and the parameters of [1970Lon, 1974Ain, 1982Rum]; the result is probably accurate to within a factor of 3 or 4.

The effect of dissolved oxygen or nitrogen impurity in the sodium was discussed in some detail [1970Lon, 1974Ain]. Although [1957Gra] claimed to have detected significantly different results with oxygen at 40 and 266 ppm, others [1970Lon, 1971Sal, 1972Sal, 1974Ain] concluded that there was no consistent difference for oxygen contents less than 450 ppm. The presence of

dissolved nitrogen, however, greatly increased the equilibration saturation concentration of C [1974Ain].

Compounds

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

- (1) simple C-Na compounds C_xNa_y ,
- (2) sodium-graphite intercalation compounds
- (3) sodium-fullerene exohedral and endohedral compounds

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

Simple C-Na Compounds C_xNa_y

C_2Na_2 (sodium acetylide, sodium carbide) may be prepared by the reaction of Na with acetylene, either directly [1866Ber, 1897Mat1, 1897Mat2, 1898Moi1, 1958Fop] or in liquid ammonia solution [1898Moi2, 1924Mel, 1999Hem]. The substance formed in liquid ammonia is C_2HNa , which, when heated in in vacuo above 100 °C yields C_2Na_2 [1898Moi1, 1963Bra, 1999Hem, 2002Klo]. It may also be prepared by the direct reaction of graphite with Na [1895For], but the reaction with acetylene is preferred. Na_2C_2 was characterized by powder XRD [1958Fop, 1973Sch, 1999Hem, 2002Klo] and neutron powder diffraction [1974Ato]. It undergoes a first-order solid state transition at 273 °C [1973Sch] or 307 °C [1999Hem] and this high-temperature form was also characterized by powder XRD [1973Sch, 1999Hem]. The melting point of Na_2C_2 is listed [1991Lid] as “about 700 °C,” but thermodynamic data [1973Joh] indicate that at high temperatures Na_2C_2 becomes unstable with respect to graphite and liquid Na.

Small C_xNa_y compounds were prepared in partial yield by the reaction of Na vapor in vacuo at 440-460 °C with chloroethane and 1,1,2,2-tetrachloroethane [1979Abr]. The products of the reaction were condensed out on a cold finger and reacted with D_2O . The completely deuterated species were identified by gas-liquid chromatography (GLC) and mass spectrometry. The existence of the species C_2Na_4 and C_2Na_6 was inferred from these experiments. Unlike the corresponding case with Li, the reaction of Na vapor with CCl_4 did not yield CNa_4 , perhaps for steric reasons [1979Abr]. Both C_2Na_4 and C_2Na_6 are apparently stable at room temperature [1979Abr]. It is to be noted that the evidence for the existence of these compounds is indirect, and they have not been prepared in quantities sufficient for characterization.

Sodium-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 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 Na-graphite intercalation compounds are

- reaction with Na vapor or liquid at low pressures
- in organic solvent solution
- reaction with liquid Na at high pressure

The preparation of compounds at high pressure is described later in the “Pressure” section of this paper. Both natural and synthetic graphite have been used in these methods.

In the reaction of graphite with Na vapor (the “two-bulb method” [1951Her1, 1957Voi]), graphite in one part of a vacuum apparatus is maintained at a given temperature and is then exposed to Na vapor from a reservoir of molten metal maintained at a lower temperature. The stoichiometry of the compound is controlled by the temperature difference between the graphite and metal reservoir. The stoichiometry, ultimately established by chemical reaction, is routinely verified by XRD [1957Voi, 1959Ash, 1975Ber]. Other techniques used are EMF [1969Aro, 1988Ge], magnetic susceptibility [1959Ash, 1966Sle], thermogravimetry [1975Ber] and dilatometry [1959Ash].

In contrast to the heavier alkali metals, Na forms graphite intercalation compounds to only a limited extent [1926Fre, 1932Sch, 1951Her2, 1954Rud, 1955Her, 1967Met, 1970Ber]. The reasons for this were considered by [1998Her]. The energetics of the process of inserting ionized Na atoms into graphite may be envisaged as steps in a Born-Haber cycle [1998Her]. The energies involved in the steps differ according to the alkali metal concerned; with Na, the overall thermodynamic balance is unfavorable.

The eighth-stage compound $C_{64}Na$ was prepared by reaction with Na vapor at temperatures above 300 °C [1961Rec, 1979Met, 1987Uen, 2002Aku]. Successful preparation was also accomplished by reaction with Na liquid [1958Ash, 1959Ash, 1969Aro] or in an electrochemical cell [1966Sle, 1985Yao, 1988Del, 1988Ge].

Lower stage compounds were obtained by reaction with Na vapor at different temperatures [1979Met]: seventh stage at 235 °C ($C_{56}Na$), sixth stage at 175 °C ($C_{48}Na$). An attempt was made to prepare a compound of stage lower than six at a lower temperature (150 °C), but the results indicated only that lower stage compounds are unstable at low pressures [1979Met].

In other studies, Na showed greater apparent reaction with other forms of carbon such as coke, soot, carbon black, activated carbon, etc. [1967Met, 1975Ber] but this behavior is due to the presence of impurities [1967Met, 1974BiI] or to simple adsorption, as shown by Brunauer-Emmett-Teller (B.E.T.) isotherms [1967Met, 1969Met, 1975Ber]. With so-called “glassy” or amorphous carbon, Na reacts to form a highly unstable material which shatters violently [1968Hal, 1969Hal].

Sodium-graphite intercalation compounds have been prepared at room temperature in tetrahydrofuran solution. The sodium is introduced as the sodium-naphthalene complex [1965Ste1, 1965Ste2, 1966Ste] or sodium-phenanthrene [1996Miz, 1997Miz]. The compounds reported are $C_{30.5\pm 1.5}Na$ and $C_{120\pm 4}Na$ [1965Ste1, 1965Ste2, 1966Ste] and a tenth-stage compound [1996Miz, 1997Miz].

Sodium-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 C_{60} (“soccer ball” shape) and C_{70} .

C_{60} may be prepared in an arc between graphite electrodes in subatmospheric Ar or He. The C_{60} 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 [1990Mej].

All the alkali metals form *exohedral* and *endohedral* compounds with fullerene. In exohedral sodium compounds, the Na atoms and fullerene molecules occupy sites on a crystalline lattice; in endohedral compounds, the Na atoms are inside the fullerene cages [1998Lah].

Exohedral compounds are usually prepared by direct reaction with Na vapor at low pressure or in an organic solvent. Preparation by direct reaction at high pressures is described in the “Pressure” section of this paper.

Direct reaction synthesis with C_{60} and C_{70} thin films was used by [1991Had] at 180 °C (stoichiometry not reported). Other compounds prepared in this way are: $C_{60}Na_6$ at 350–400 °C [1992Mur, 1992Ros] and $C_{60}Na_x$ ($x = 7.2, 9, 11, 12$) at 300 °C [1992Yil]. $C_{60}Na_{1.3}$ was prepared by dilution of $C_{60}Na_9$ [1993Yil].

Decomposition of NaN_3 provided sodium in preparations of $C_{60}Na$ at 390–440 °C [1999Yas] and $C_{60}Na_4$ at 200–400 °C [1997Osz]. The compound $C_{60}Na_4$ transforms at about 500 K to a mixture of two solid phases of different crystalline structure [1998Osz].

$C_{60}Na_2$ was prepared by the reaction between NaH and C_{60} and $C_{60}Na_3$ from Hg_2Na_5 + C_{60} [1992Mur, 1992Ros].

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All compounds prepared by direct reaction in absence of solvent were characterized by XRD.

Direct reaction between Na and C₆₀ or C₇₀ in toluene solution occurs at 110-130 °C or RT either with or without previous high-energy milling of the mixtures. The compounds are insoluble in the solvent and precipitate; the reaction is followed by monitoring the concentration of fullerene by infrared absorption spectrophotometry. The stoichiometry was established gravimetrically. In this manner were prepared C₆₀Na and C₇₀Na [1995Bez, 1996Bez], C₆₀Na₃ [1998Bul, 1998Dit, 2000Dyt] and C₆₀Na₆ [2000Dyt]. In the latter work, the reaction was monitored by recording ¹³C and ²³Na NMR peaks. Compounds prepared this way were not characterized.

The Na-C₆₀ endohedral compound is conventionally indicated as Na@C₆₀. Thin films of this compound were produced by low-energy bombardment of C₆₀ with Na⁺ ions. The films were characterized by laser desorption spectrometry as well as infra-red (IR) and Raman spectroscopy [1996Cam, 1996Tel].

Crystal Structures and Lattice Parameters

These are presented in Tables 3 and 4 respectively.

The structure of both forms of C₂Na₂ were determined from powder XRD [1958Fop, 1973Sch, 1999Hem]. In α-C₂Na₂ the C₂²⁻ ions were described as “distorted ellipsoids” in which the C-C distance is 0.12 nm [1958Fop]. The tetragonal structure of α-C₂Na₂ was described [1999Hem] as a distorted variant of the anti-fluorite type (Z = 8). The structure of β-C₂Na₂ is cubic (Z = 4) [1999Hem]. Another high-temperature modification was discovered [2002Klo] which proved to be metastable. For this orthorhombic structure (space group Immm, Z = 2), the lattice parameters were a = 0.41893 nm, b = 0.64007 nm, c = 0.53862 nm at ambient temperature. The metastable form is isostructural with C₂Li₂ and Rb₂O₂.

The structure of the graphite intercalation compound C₆₄Na (stage VIII) is closely derived from that of graphite. The XRD results of [1959Ash] were indexed by [1960Wol] on the basis of an orthorhombic unit cell, space group C222 (or F_{ddd}). Later more refined calculations (summarized in [1979Her]) suggested that hexagonal symmetry better accounted for the data. In C₆₄Na the interlayer distances (Fig. 2, nomenclature of [1971Nov]) are: I_c (identity or repeat period) = 2.8 nm; I_c (thickness of a filled layer) = 0.45 nm; I_c (thickness of an unfilled layer) = 0.335 nm (as it is in pure graphite) [1959Ash].

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 lattice was deduced from powder XRD [1990Kra, 1991Hei]. Originally it was thought that the spheres were stacked in a hexagonal close-packed lattice, with 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 sodium fullerides C₆₀Na₂, C₆₀Na₃ and C₆₀Na₆ are fcc at ambient temperature [1992Ros]. The Na atoms in these crystals occupy tetrahedral sites. A particularly full account of the structure of these compounds is given by [1992Mur]. Non-stoichiometric compounds include C₆₀Na_{9.7} (fcc, a = 1.459 nm) [1992Yil] and C₆₀Na_{1.3} (fcc,

Table 3 C-Na crystal structure data

Phase	Composition, at.% Na	Pearson symbol	Space group	Strukturbericht designation	Prototype	Reference
C	0	<i>hP4</i>	<i>P6₃/mmc</i>	A9	C (graphite)	[King1]
C	0	<i>cF8</i>	<i>Fd$\bar{3}m$</i>	A4	C (diamond)	[King1]
C	0	<i>cF240</i>	<i>Fm$\bar{3}m$</i>		C ₆₀	[1991Hei]
C ₆₀ Na	1.6	<i>cF*</i>				[1999Yas]
C ₆₄ Na	1.5	<i>h**</i>				[1959Ash]
C ₆₀ Na ₂	3.2	<i>cF248</i>	<i>Fm$\bar{3}m$</i>			[1992Ros]
C ₆₀ Na ₃	4.8	<i>cF252</i>	<i>Fm$\bar{3}m$</i>			[1992Ros]
C ₆₀ Na ₄	6.3	<i>mI*</i>	<i>I2/m</i>			[1997Osz]
C ₆₀ Na ₆	9.1	<i>cF280</i>	<i>Fm$\bar{3}m$</i>			[1992Ros]
α-C ₂ Na ₂	50.0	<i>tI32</i>	<i>I4₁/acd</i>			[1958Fop, 1973Sch]
β-C ₂ Na ₂ (a)	50.0	<i>cF16</i>	<i>Fm$\bar{3}m$</i>			[1973Sch, 1999Hem]
α-Na (b)	100	<i>hP2</i>	<i>P6₃/mmc</i>			[King2]
β-Na	100	<i>cI2</i>	<i>Im$\bar{3}m$</i>	A2	W	[King2]

(a) Above 273 °C, (b) Below 237 °C

Table 4 C-Na lattice parameter data

Phase	Composition, at.% Na	Lattice parameter, nm			Comment	Reference
		<i>a</i>	<i>b</i>	<i>c</i>		
C (dia)	0	0.54308				[Pearson3]
C (graphite)	0	0.2464		0.6711		[Pearson3]
C (C ₆₀)	0	1.411				[1991Ste]
		1.4161				[1992Tan]
		1.417				[1991Hei]
		1.4172				[1991Fle]
		1.4155				[1992Aga]
C ₆₀ Na	0.02	1.420				[1999Yas]
C ₆₀ Na ₂	3.2	1.4189				[1992Mur, 1992Ros]
C ₆₀ Na ₃	4.8	1.4191				[1992Ros]
		1.4183				[1992Mur]
C ₆₀ Na ₄	6.3	1.124	1.172	1.028	β = 96.2°	[1997Osz]
C ₆₀ Na ₆	9.1	1.4381				[1992Ros]
		1.4380				[1992Mur]
α-C ₂ Na ₂	50	0.6756		1.2688		[1958Fop, 1973Sch]
		0.6778		1.274		[1999Hem]
		0.6743		1.2674		[1974Ato]
β-C ₂ Na ₂ (a)	50	0.671				[1973Sch]
(b)		0.6756				[1999Hem]
α-Na (c)	100	0.3767		0.6154		[King2]
β-Na	100	0.42906				[King2]

(a) At 276 °C, (b) At 477 °C, (c) At <-237 °C

$a = 1.4184$ nm [1993Yil]. C₆₀Na₄ transforms at ~500 K to a mixture of two solids, the major component of which is bct, with $a = 1.1731$ nm and $c = 1.0438$ nm; the minor component is fcc, with a ~1.436 nm [1998Osz].

Theoretical calculations [1996And, 1997Apo, 2005Pit] and measurements of electric polarizability [2001Dug] and dipole moment [2000Ant] suggest that sodium fullerides are partially ionic in nature.

Endohedral compounds have been prepared only as thin films, and no crystalline structure data are available. Since the Na atoms are inside the C₆₀ cages, it is expected that the crystalline structure of Na@C₆₀, for example, would be very similar to C₆₀ itself.

Thermodynamics

The standard enthalpy of formation of α-C₂Na₂ was determined to be 16 or 15 kJ/mol from reaction calorimetry in two early investigations [1895For, 1897Mat2]. A recent result by the same method is 20.1 kJ/mol [1973Joh], and a standard compilation [1982Wag] lists 17.2 kJ/mol (no discussion, no source stated). The heat capacity of α-C₂Na₂ was measured in the interval 6-348 K [1973Joh] and the equation given by these authors for the range -25 to +75 °C is

$$C_p = 73.68 + 6.711E - 2T - 2.42E5T^{-2} \quad \text{J/mol} \cdot \text{K}^{-1}$$

where T is in Kelvin. The third-law entropy of α-C₂Na₂ is 111.24 J/mol·K⁻¹ [1973Joh]. The enthalpy of transition for

α-C₂Na₂ → β-C₂Na₂ was estimated to be 4.2 kJ/mol, based on the entropy of transition of CaC₂ [1973Joh].

Thermodynamic properties of formation of alkali metal graphite intercalation compounds were reviewed by [1959Hen, 1968Tak, 1971Nov, 1979Her]. The evident scarcity of sodium compounds at ordinary temperatures and pressures suggests that the Gibbs energy of formation of these compounds is positive; this was rationalized in terms of ionization potentials of the intercalating metal [1959Hen]. Other authors cite kinetic factors for the apparent difficulty of Na in entering the graphite lattice [1961Rec].

The enthalpy of formation of exohedral sodium fullerides was calculated by the Born-Haber cycle. For C₆₀Na₂ the value is -178 kJ/mol [1996Cla]; for C₆₀Na₃, -140 kJ/mol [1993Tom]; for C₆₀Na₆, -121 kJ/mol [1993Tom].

The same method was used for endohedral Na@C₆₀ (-149 kJ/mol) [1993Wan].

Pressure

Although only high-stage Na-graphite intercalation compounds can be obtained by synthesis at low pressure, high pressure has been used to synthesize lower-stage compounds. These syntheses were not done in a systematic manner because interest was mainly focused on superconductivity. The direct reaction of graphite with liquid Na was carried out at temperatures greater than 250 °C and pressures greater than 15 kbar. In those reports which

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quoted a stoichiometry, these were C_xNa , where $x = 1.54$ [1990Avd], 2 [1989Bel, 1994Udo], 2.6 [1990Nal, 1992Nal], 2.69 [1990Avd], 3 [1989Bel], 4.5 [1989Sya], 8-9 [1989Sya]. These were Stage I or Stage II compounds. Other authors simply stated the Stage numbers: III and IV [1982Avd, 1982Mor], VI and VII [1980Bil]. The materials were characterized by one or more of the following: XRD, Raman spectroscopy, reflectivity, magnetic susceptibility, DTA and electrical conductivity.

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, 1996Mar, 1998Dav, 1999Mar]. Sodium fullerenes are similarly affected. $C_{60}Na_x$ ($x = 1-3$) compounds under pressure treatment yielded trigonal structures [1999Yas]. In particular, the trigonal lattice parameters for $C_{60}Na$ treated at 5 GPa and 300 °C were $a = 0.931$ nm, $c = 2.47$ nm.

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