

Short Communications

Phase Equilibria in Aluminum-Carbon System at High Temperatures

Editor's Note: This communication is an abbreviated version of a paper that will be published in its entirety in *Ber. Bunseng. Phys. Chem.*, Vol 102 (1998), but a delay is expected before that occurs. Timely dissemination of information about important systems justifies publication of this short report.

A number of phase diagrams have recently been presented for the Al-C system, all below 2800 K [87Ode, 90Mas, 91Har, 91Sch, 92Oka, and 94Qiu]. These diagrams are, for the most part, concordant, but possible disagreements have been noted by [92Oka]. Experimental results of [65Gin], [68Gje], and [87Ode] are particularly concordant, and thermodynamic interpretations and constructions by [91Har], [94Qiu], and [97Ode] are in reasonable agreement. The main purpose of this article is to complete the thermodynamic interpretations of Al-C equilibria and to extend the diagram beyond 2800 K at 1 bar to include the gas-condensed phase regions and to present a phase diagram at 1 bar of pressure.

Requisite thermodynamic equations are presented in [94Gok] and [97Ode]. Briefly, the partial Gibbs energy of carbon in liquid solution is expressed as:

$$G_2(y, T, L) = G_2^0(T, \text{gr.}) + RT \ln a_2 \quad (a_2 = \gamma_2) \quad (\text{Eq 1})$$

where G_2^0 is the standard molar Gibbs energy of graphite (gr), R and T are the gas constant and the temperature in K, respectively, a_2 is the activity of dissolved carbon, which is equal to the mol fraction y times the activity coefficient γ_2 , based on graphite as the standard state. Equation 1 may be rewritten by taking the supercooled liquid carbon as the standard state and writing $\gamma_2(L)$ as the corresponding activity coefficient; thus:

$$G_2(y, T, L) = G_2^0(T, L) + RT \ln a_2(L) \quad [a_2(L) = \gamma_2(L)] \quad (\text{Eq 2})$$

The left sides of Eq 1 and 2 refer to the same component at the same value of y and the same liquid alloy phase, and they are equal; therefore:

$$G_2^0(T, L) - G_2^0(T, \text{gr.}) \equiv \Delta G_2^0(\text{melt}) = RT \ln [\gamma_2/\gamma_2(L)] \quad (\text{Eq 3})$$

where $\Delta G_2^0(\text{melt})$ is the standard Gibbs energy of melting of graphite. The excess partial Gibbs energy of carbon, $G_2^{\text{ex}}(L)$ is related to $\gamma_2(L)$ and the mol fraction x of Al by the quadratic Margules equation [86Gok]; that is:

$$G_2^{\text{ex}}(L) \equiv RT \ln \gamma_2(L) = Ax^2 \quad (\text{Eq 4})$$

where A is a function of T . The substitution of Eq 4 in 3, and the rearrangement of result yields:

$$G_2^{\text{ex}} \equiv RT \ln \gamma_2 = \Delta G_2^0(\text{melt}) + Ax^2 \quad (\text{Eq 5})$$

Here, γ_2 , hence G_2^{ex} , is the usual experimentally measured value, based on graphite as the standard state. It is very important to observe that A is for the liquid solution, and independent of the choice for the state of aggregation of standard state.

The melting point of graphite was determined with a continuous HF-laser as 4130 K by [76Gok]. An estimated value of entropy of fusion is 30 for the carbon group elements; the enthalpy of melting is therefore $4130 \times 30 = 123\,900$ J/mol. An estimated value of the heat capacity change for melting, again for the carbon group elements, is -3.0 J/mol · K. These values yield, in J/mol [94Gok]:

$$\Delta G_2^0(\text{melt}) = 136\,290 - 57.98T + 3.0T \ln T \quad (\text{Eq 6})$$

The solubility of Al_4C_3 in liquid Al, obtained by [87Ode] and represented in Fig. 1, was used by [97Ode], with critically assessed data tabulated by [95Pan] for the standard Gibbs energy

of formation of Al_4C_3 to derive the equations for G_1^{ex} and G_2^{ex} at T less than 2429 K.

At $T = 2430$ to 2800 K, the resulting data of $\gamma_2 = 1/y$ at carbon saturation is fit to Eq 5. The results obtained by [97Ode], based on $y = 0.1886$ at 2429 K and $y = 0.288$ at 2800 K, are:

$$G_2^{\text{ex}} = x^2 (-63\,170 + 14.4T) + 136\,290 - 57.98T + 3.0T \ln T \quad (\text{Eq 7})$$

$$G_1^{\text{ex}} = y^2 (-63\,170 + 14.4T) \quad (\text{Eq 8})$$

where G_1^{ex} is the excess partial Gibbs energy of Al. The value of y at saturation was obtained by using a large plot of the data by [68Gje], which were considered to be more reliable than the older data of [34Bau]. The latter data scatter more, and on the average, they are about 10% lower than those by [68Gje], but support the data plotted in Fig. 1.

Phase Diagram at 1 bar

Equations 7 and 8 are used in constructing the phase diagram in Fig. 1, at 1 bar. The carbon saturation liquidus follows Eq 7 from 2429 to 2900 K. The bubble-point curve (or the boiling curve) from $y = 0$ to 0.30 were calculated by using the vapor pressure of P_1^0 (in bars) of pure Al(L), obtained by fitting the tabular data of [85Cha] with the following equation:

$$\Delta G_1^0 = -RT \ln P_1^0 = 324\,553 + 10.9448T \ln T - 203.131T \quad (\text{Eq 9})$$

This equation accurately represents ΔG_1^0 for $\text{Al}(L) = \text{Al}(g)$ at temperatures above 2790.812 K, for which there are no tabular data. The activity of Al, a_1 , is given by:

$$RT \ln a_1 = G_1^{\text{ex}} + RT \ln x = y^2 (-63\,170 + 14.4T) + RT \ln x \quad (\text{Eq 10})$$

At a constant Al(g) pressure of 1 bar over the solution $a_1 = 1/P_1^0$. Thus, one writes $RT \ln a_1 = -RT \ln P_1^0$ between Eq 9 and 10, and for a selected value of x the value of T can be solved by successive approximations in Eq 9 = Eq 10. As an example, $T = 2849.5$ is obtained for the selected value $x = 0.80$. This is a typical example of the "elevation of boiling point" [96Gok] by the dissolution of carbon, which has a much lower vapor pressure at these temperatures than aluminum. The calculation of such points, plotted in Fig. 1, yields the "bubble-point curve," that is, the "boiling curve" of the Al-rich solutions. The elevation of the boiling points necessitates that the $(G + L)/L$ boundary must curve upward as indicated.

The graphite saturation curve was calculated from Eq 7 with $G_2^{\text{ex}} + RT \ln y = RT \ln a_2 = 0$. The intersection of

this curve with the bubble-point curve yields the tectoid-type point corresponding to $(\text{gas} + \text{graphite} \rightarrow \text{liquid})$ transformation temperature, shown as 2900 K and $y = 0.319$. Any errors in Eq 6 and 7 would change the liquid boundary curves and the invariant point, without affecting their basic forms.

The remaining section above 2900 K contains the gas-phase consisting of $\text{Al(g)} + C_i(\text{g})$, where i ranges from 1 to 5, and at high temperatures, C_3 is the major gas species. It was assumed that the graphite phase is very nearly pure in the absence of solid solubility data, and at each temperature, the authors computed the total gas pressure of the species from [85Cha]. This pressure, plus Al(g) pressure, constitutes 1 bar at each temperature, and the resulting composition of $[\text{Al(g)} + C_i(\text{g})]$ is plotted as the upper curve. The sublimation point of graphite is 4080 K, from [85Cha]. This

completes the Al-C phase diagram at 1 bar of pressure.

The sublimation point of 4080 K is based on the equilibrium pressure measurements at lower temperatures extrapolated to far higher temperatures. These measurements are not in accord with those by [76Gok]. Nevertheless, the general form of the gas/(gas + graphite) boundary is valid and would move up or down depending on the equilibrium vapor pressure of graphite. Clearly, far more reliable measurement of the vapor pressure of graphite is needed for a more reliable representation of the gas phase boundaries above 3000 K.

Under sufficiently high pressures, for example, about 200 bars, only the condensed phases can coexist. The activity of C in the liquid phase is unity so that from G_2^{ex} of Eq 7 and $a_2 = \gamma_2 y = 1$ one obtains $RT \ln a_2 = G_2^{\text{ex}} + RT \ln y = 0$. For each selected value of temperature, $G_2^{\text{ex}} + RT \ln y = 0$ can be solved for y by successive approximations. The results represent the extension of the liquidus $L/(L + \text{Gr})$ boundary of 2429 to 2900 K all the way up to the triple point of graphite, which is 4130 K; that is, the liquidus terminates at 4130 K and $y = 1$ (not shown here). The triple point of pure graphite was taken from [76Gok] as 4130 K, and roughly 122 ± 10 bars. In such measurements by [76Gok], it was impossible to obtain liquid carbon below 122 bars when various pressurization gases were used. The general form of this curve is valid even if the triple point is moved up or down.

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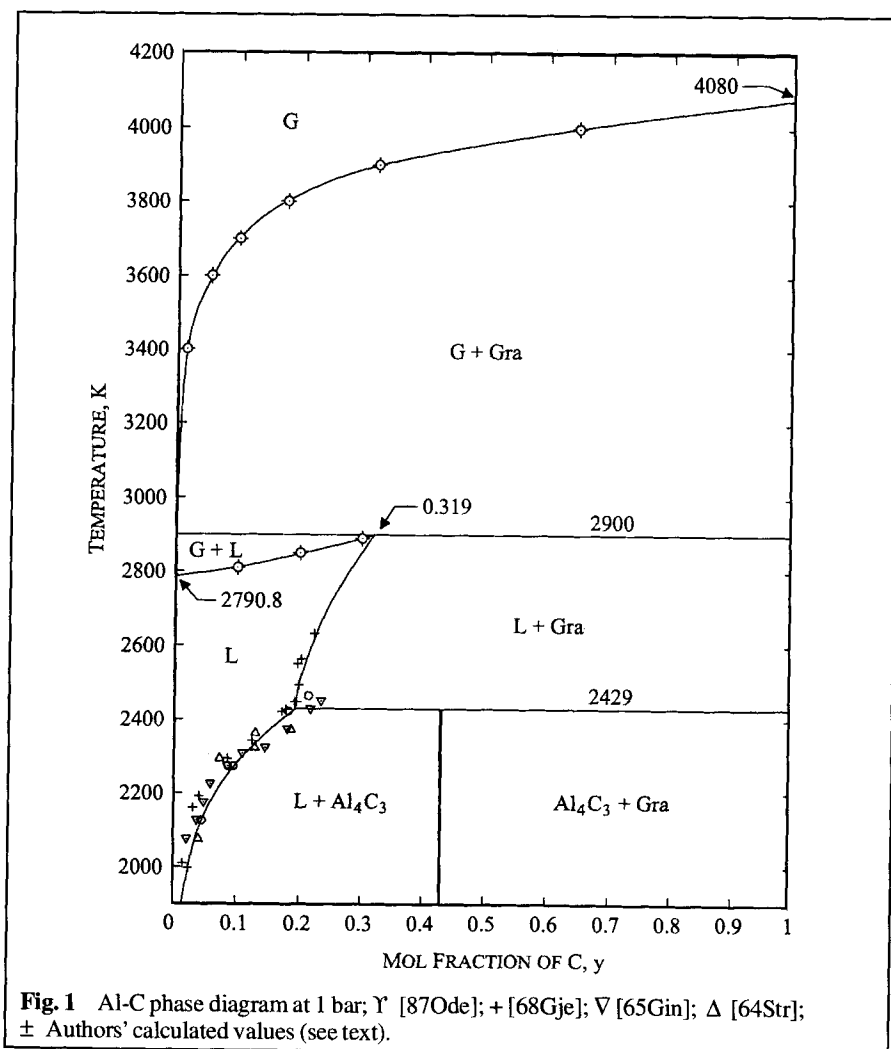


Fig. 1 Al-C phase diagram at 1 bar; \circ [87Ode]; $+$ [68Gje]; ∇ [65Gin]; Δ [64Str]; \pm Authors' calculated values (see text).

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