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Thermodynamics of the Al_2O_3–Al_4C_3 system I. Thermochemical functions of Al oxide, carbide and oxycarbides between 298 and 2100 K

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Abstract

A consistent set of thermochemical functions are proposed for aluminium oxide (Al_2O_3), carbide (Al_4C_3) and oxycarbides (Al_4O_4C, Al_2OC), including Gibbs free energies, enthalpies and entropies of formation as well as heat capacities, between 298 and 2100 K. Heat capacities of the base components of the Al–O–C system are also given. All equations are compared with existing functions in terms of relative errors, pointing important discrepancies for aluminium carbide and aluminium oxycarbide Al_2OC. When some are used to determine equilibrium partial pressures of carbon monoxide in classical high temperature solid–gas reactions, these discrepancies are confirmed or amplified. As a consequence, the present equations are suggested to describe the thermodynamic behaviour of aluminium carbide and aluminium oxycarbide Al_2OC.

Keywords: Chemical properties; Al_2O_3; Carbides; Aluminium oxycarbides; Refractories; Al_4C_3; Thermodynamic data

1. Introduction

Aluminium carbide (Al_4C_3) is a quite interesting material, although its high reactivity with water precludes its use in many instances. It forms readily when previously and sufficiently mixed and milled elemental powders of aluminium and graphite are heated in Argon above some hundreds of degrees.[1] It has also been observed to form at room temperature, as 2–4 nm grain size precipitates, by implantation of carbon ions into pure aluminium, though at a carbon concentration below the stoichiometric value.[2] Whereas Al_4C_3 is currently being used as a surrogate for beryllium carbide in the tokamak dust particle removal studies,[3] it is also a soft reactant for Al_2O_3, able to form two Al oxycarbides which act as very efficient binding agents in 95^+% Al_2O_3 refractory bricks, with higher thermal resistance, mechanical strength and abrasive properties than the classical graphite, mullite and sialon binders.[4,5] Furthermore, the thermodynamic properties of Al_4C_3 are very important in the case of Al/SiC metal matrix composites since they inform on the possible formation of this compound at Al/SiC interfaces, where it is indeed frequently observed, without omitting to mention the high catalytic ability of Al_4C_3 particles to nucleate α-Al phase in hypoeutectic Al–Si alloys.[6] While on the other hand aluminium oxide offers a multitude of industrial applications as a major ceramic material,[7] the present paper is aimed at updating the various thermochemical functions of the solid compounds within the Al_2O_3–Al_4C_3 system. In this purpose, a set of equations are at first proposed and compared with previously suggested equations, then the improvements are shown by investigating their implications on some high temperature reactions often encountered in the carbothermal reduction of alumina.

2. Rationale

The stable phase-equilibrium diagram of the Al_2O_3–Al_4C_3 system is presented in its usual form in Fig. 1. It features both oxycarbides as intermediate compounds,[8] the richer in Al_2O_3 decomposing peritectically at 2163 K while the equimolar compound is stable between a eutectoid plateau slightly above 1983 K and a peritectic plateau near 2260 K; this diagram also includes a eutectic reaction about 2123 K. The solubilities of all four compounds, which are not represented in Fig. 1, are dis-

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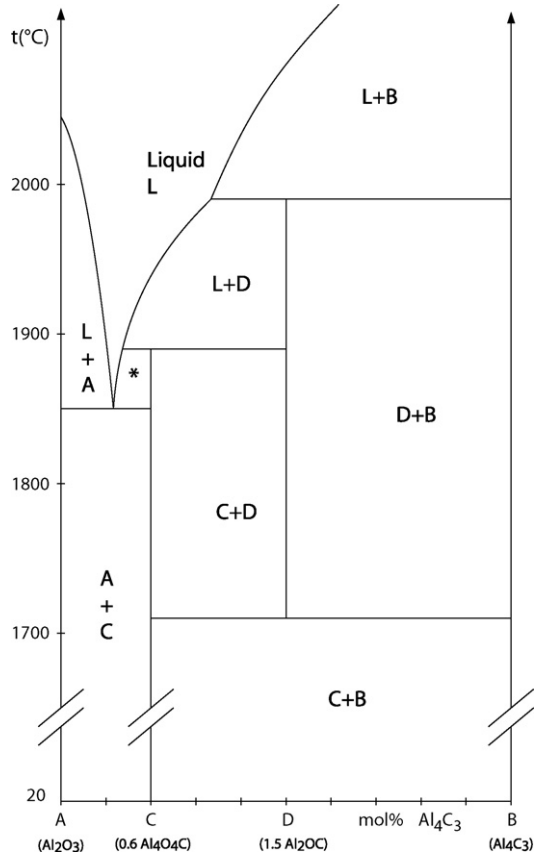

Fig. 1. Phase diagram of the Al_2O_3–Al_4C_3 system (* = L + C).

cussed in Part 2 of this work and are shown to be negligibly small. As it is often the case in ceramic systems,[9] there exists in addition a metastable Al_2O_3–Al_4C_3 diagram,[8,10,11] which is observed for higher cooling rates and not referred to in the present study.

A previous paper[12] listed the Gibbs free energies of formation of these compounds between 1000 and 2100 K. In a first step, these functions were extended to the melting temperature of aluminium (933 K), and the enthalpies and entropies of formation of solid compounds were obtained, as well as their heat capacities, once those of the base components $C_{(s)}$, $Al_{(l)}$ and $O_{2(g)}$ were defined between 933 and 2100 K. In a second step, heat capacities of both solid compounds and base components were defined between 298 and 933 K, what permitted to determine enthalpies, entropies and Gibbs free energies of formation of all solid compounds in this interval; the molar heat of fusion of aluminium was taken as 10,500 J.

Aluminium oxycarbides are not widely used so far, nor are the thermodynamic properties of aluminium carbide often discussed or in question, so that the references available for comparison are altogether rather scarce.[13–17]

3. Results

All equations suggested in this section concern standard properties (normal pressure), in SI units (J, mole, K), of solids in their field of thermodynamic stability, whence the narrow temperature range for Al_2OC: 1983.05–2100 K; usually, three

Table 1
Standard Gibbs free energies of formation of solid compounds in the C–Al–O system, in SI units (J, mole, K)

Al_2O_3		
$298 \le T \le 933$		
	$\Delta_f G^\circ = -1692098.49628 + 469436.372462 \times 10^{-3}\,T - 20.79\,T \ln T - 1087.525 \times 10^{-6}\,T^2 + 2911.2095 \times 10^{-9}\,T^3 + 1506.970625 \times 10^3/T$	(1)
$933 \le T \le 1500$		
	$\Delta_f G^\circ = -1703587.779 + 362016.573 \times 10^{-3}\,T - 2320.216 \times 10^{-3}\,T \ln T - 5438.306 \times 10^{-6}\,T^2 + 258.189 \times 10^{-9}\,T^3 + 1331.985 \times 10^3/T$	(2)
$1500 \le T \le 2100$		
	$\Delta_f G^\circ = -1750864.909 + 660614.800 \times 10^{-3}\,T - 42120.216 \times 10^{-3}\,T \ln T + 8878.444 \times 10^{-6}\,T^2 - 649.745 \times 10^{-9}\,T^3 + 11577.935 \times 10^3/T$	(3)
Al_4C_3		
$298 \le T \le 933$		
	$\Delta_f G^\circ = -198954.518109 - 78152.2033574 \times 10^{-3}\,T + 19.20\,T \ln T - 26031.6 \times 10^{-6}\,T^2 + 9815.3473333 \times 10^{-9}\,T^3 - 5908.882 \times 10^3/T + 792.9 \times 10^6/T^2 - 36 \times 10^9/T^3$	(4)
$933 \le T \le 2100$		
	$\Delta_f G^\circ = -209944.693 - 282185.012 \times 10^{-3}\,T + 51158.268 \times 10^{-3}\,T \ln T - 15316.705 \times 10^{-6}\,T^2 + 0.3633 \times 10^{-9}\,T^3 - 9551.482 \times 10^3/T + 792.9 \times 10^6/T^2 - 36 \times 10^9/T^3$	(5)
Al_4O_4C		
$298 \le T \le 933$		
	$\Delta_f G^\circ = -2334566.14257 + 612528.342841 \times 10^{-3}\,T - 22.98\,T \ln T - 10800.5 \times 10^{-6}\,T^2 + 7730.60066667 \times 10^{-9}\,T^3 - 44.5975 \times 10^3/T + 264.3 \times 10^6/T^2 - 12 \times 10^9/T^3$	(6)
$933 \le T \le 1500$		
	$\Delta_f G^\circ = -2352531.936 + 388627.099 \times 10^{-3}\,T + 13959.135 \times 10^{-3}\,T \ln T - 12356.643 \times 10^{-6}\,T^2 + 344.37 \times 10^{-9}\,T^3 - 1407.847333 \times 10^3/T + 264.3 \times 10^6/T^2 - 12 \times 10^9/T^3$	(7)
$1500 \le T \le 2100$		
	$\Delta_f G^\circ = -2415568.109 + 786758.068 \times 10^{-3}\,T - 39107.532 \times 10^{-3}\,T \ln T + 6732.357 \times 10^{-6}\,T^2 - 866.2056 \times 10^{-9}\,T^3 + 12253.41934 \times 10^3/T + 264.3 \times 10^6/T^2 - 12 \times 10^9/T^3$	(8)
Al_2OC		
$1983.05 \le T \le 2100$		
	$\Delta_f G^\circ = -667653.2006 + 300380.064 \times 10^{-3}\,T - 19187.316 \times 10^{-3}\,T \ln T - 2146.087 \times 10^{-6}\,T^2 - 216.4606 \times 10^{-9}\,T^3 + 675.484334 \times 10^3/T + 264.3 \times 10^6/T^2 - 12 \times 10^9/T^3$	(9)

Table 2
Standard heat capacities of the base components in the system C–Al–O, in SI units (J, mole, K)

C (graphite)

$298 \le T \le 2100$

$$C_p^\circ = 24.3 + 0.9446 \times 10^{-3}\,T - 5.1252 \times 10^6/T^2 + 1.5858 \times 10^9/T^3 - 0.144 \times 10^{12}/T^4 \quad (28)$$

Al

$298 \le T \le 933$

$$C_p^\circ = 29.095 - 9.57485 \times 10^{-3}\,T + 15.872946 \times 10^{-6}\,T^2 - 0.268741 \times 10^6/T^2 \quad (29)$$

$933 \le T \le 2100$

$$C_p^\circ = 31.750 \quad (30)$$

O_2

$298 \le T \le 933$

$$C_p^\circ = 21.42 + 22.6769 \times 10^{-3}\,T - 9.519090 \times 10^{-6}\,T^2 + 0.1804845 \times 10^6/T^2 \quad (31)$$

$933 \le T \le 1500$

$$C_p^\circ = 34.47 + 1.8412 \times 10^{-3}\,T - 1.455811 \times 10^6/T^2 \quad (32)$$

$1500 \le T \le 2100$

$$C_p^\circ = 34.717 + 1.730 \times 10^{-3}\,T - 1.6352695 \times 10^6/T^2 \quad (33)$$

Table 3
Standard heat capacities of the solid compounds in the system C–Al–O, in SI units (J, mole, K)

Al_2O_3

$298 \le T \le 933$

$$C_p^\circ = 111.11 + 17.0407 \times 10^{-3}\,T - 3.2806965 \times 10^6/T^2 \quad (34)$$

$933 \le T \le 1500$

$$C_p^\circ = 117.525216 + 13.638412 \times 10^{-3}\,T - 1.549134 \times 10^{-6}\,T^2 - 4.8476865 \times 10^6/T^2 \quad (35)$$

$1500 \le T \le 2100$

$$C_p^\circ = 157.695716 - 15.161888 \times 10^{-3}\,T + 3.89847 \times 10^{-6}\,T^2 - 25.60877425 \times 10^6/T^2 \quad (36)$$

Al_4C_3

$298 \le T \le 933$

$$C_p^\circ = 170.08 + 16.5976 \times 10^{-3}\,T + 4.5997 \times 10^{-6}\,T^2 - 4.6328 \times 10^6/T^2 \quad (37)$$

$933 \le T \le 2100$

$$C_p^\circ = 148.741732 + 33.46721 \times 10^{-3}\,T - 2.1798 \times 10^{-9}\,T^2 + 3.727364 \times 10^6/T^2 \quad (38)$$

Al_4O_4C

$298 \le T \le 933$

$$C_p^\circ = 206.50 + 29.60 \times 10^{-3}\,T - 1.93 \times 10^{-6}\,T^2 - 5.75009 \times 10^6/T^2 \quad (39)$$

$933 \le T \le 1500$

$$C_p^\circ = 206.280865 + 29.340286 \times 10^{-3}\,T - 2.06622 \times 10^{-6}\,T^2 - 5.221127334 \times 10^6/T^2 \quad (40)$$

$1500 \le T \le 2100$

$$C_p^\circ = 259.841532 - 9.060114 \times 10^{-3}\,T + 5.1972336 \times 10^{-6}\,T^2 - 32.90257768 \times 10^6/T^2 \quad (41)$$

Al_2OC

$1983.05 \le T \le 2100$

$$C_p^\circ = 124.345816 + 6.101774 \times 10^{-3}\,T + 1.2987636 \times 10^{-6}\,T^2 - 7.293803418 \times 10^6/T^2 \quad (42)$$

temperature intervals are distinguished: 298–933, 933–1500 and 1500–2100 K.

Gibbs free energies of formation of solid compounds are listed in Table 1; the corresponding enthalpies and entropies of formation, readily derived from the former, are listed in Tables A.1 and A.2 (see Appendix A).

Heat capacities of base components are listed in Table 2; those of solid compounds are in Table 3 and illustrated in Fig. 2. Eqs. (35), (36), (38), (40), (41) and (42) were obtained using appropriate functions of Table A.1 as well as Eqs. (28), (30), (32) and (33); below 933 K, Eqs. (28), (29), (31), (34), (37) and (39) were necessary to determine the low temperature functions of Tables A.1, A.2 and 1. Eq. (28) is suggested[18] by SGTE and Eq. (30) is in close agreement with numerous references. Eq. (32) through (34), which obey the most classical form for a heat capacity function,[19] were obtained from Janaf[15] data, in addition with Refs. 13 and 14 for Eq. (34). The remaining equations include an additional quadratic term; they were obtained using data from Janaf[15] for (29), (31) and (37), and from Ref. 13 for (37) and (39).

4. Discussion

Eq. (1) through (9) establish that Al_4O_4C oxycarbide is a more stable compound than Al_2O_3, itself more stable than Al_2OC and finally Al_4C_3; on a unit constituent basis, 1/5 Al_2O_3 is more stable than 1/9 Al_4O_4C, itself more stable than 1/4 Al_2OC and finally 1/7 Al_4C_3 (see Part 2).

Among all equations of Tables 1, A.1 and A.2, those which are closely approximated by linear functions are compared

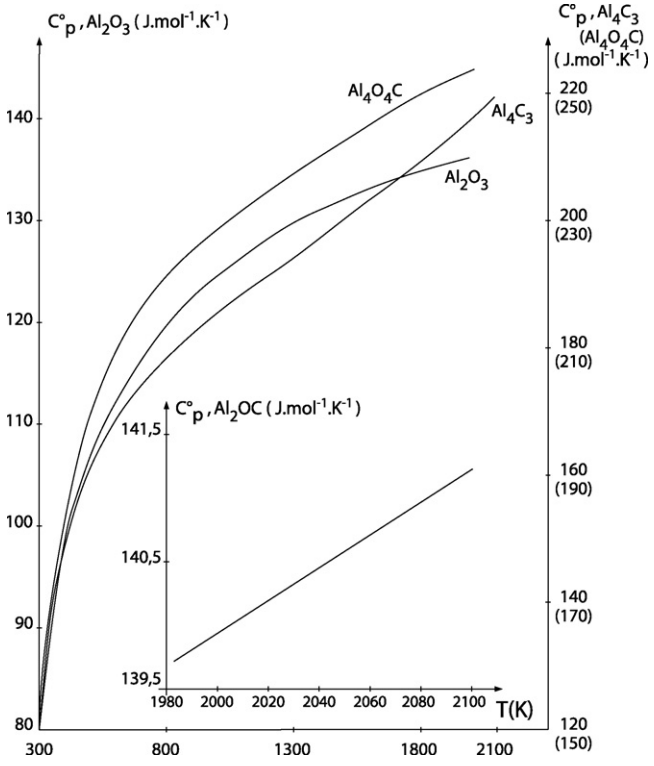

Fig. 2. Calculated heat capacities (J mol^{-1} K^{-1}) of solid compounds Al_2O_3, Al_4C_3, Al_4O_4C and Al_2OC between 300 and 2100 K.

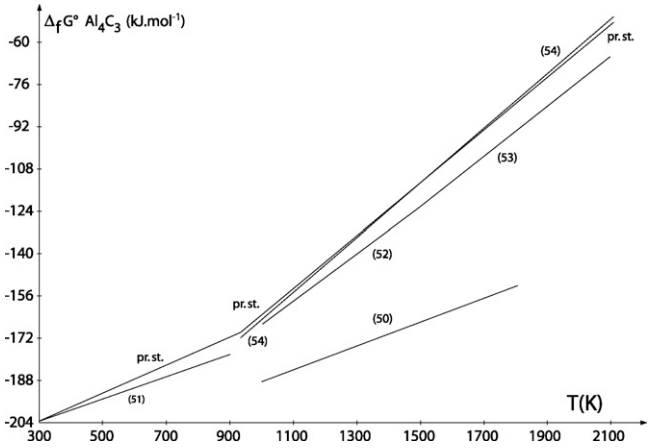

Fig. 3. Gibbs free energies of formation of aluminium carbide.

with their linear counterparts in Table A.3. It appears that 9 among the 10 functions describing Gibbs free energies of formation are perfectly linear, thereby verifying, over fairly extended temperature intervals, Ülich approximation of nearly temperature-independent enthalpies and entropies of reactions; this approximation is more thoroughly studied in Appendix A (Table A.4). The last $\Delta_f G^\circ$ function may be said to be close to linear with a high accuracy, and so are the various $\Delta_f S^\circ$ equations listed in the table; this statement becomes somewhat less true for the standard enthalpies of formation. It can also be seen that the relative errors between each function and its linear approximation are extremely small at all temperatures, most of them smaller than $\pm 2.5 \times 10^{-2}$% and never exceeding either −0.1295% or +0.2582%.

Other existing equations for Gibbs free energies, enthalpies and entropies of formation of the solid compounds in the C–Al–O system, as mentioned in Refs. 14 through 17, are listed in Tables 4 and 5. Eq. (56) through (59) were derived from Eqs. (43) and (44), and all functions numbered with a superscript are linear estimates of discrete data from Ref. 15. Table A.5 shows that the relative errors between estimates and data do not exceed ±0.321%.

These other existing functions are compared with those of Tables 1, A.1 and A.2 in Table 6 (here all Janaf data used for comparison are the actual values, rather than the modelled ones; the same also applies for Table 9). It clearly appears that the situation with aluminium carbide is very different from that of aluminium oxide and aluminium oxycarbide Al_4O_4C. With

Table 4
Other existing functions for Gibbs free energies of formation of solid compounds in the C–Al–O system, in SI units (J, mole, K)

		References
Al_2O_3		
$298 \le T \le 933$, $\Delta_f G = -1676989.04 + 366.68576\,T - 16.65232\,T \log T$	(43)	14
$933 \le T \le 1800$, $\Delta_f G = -1697699.84 + 385.8485\,T - 15.69\,T \log T$	(44)	14
$298 \le T \le 900$, $\Delta_f G^\circ = -1674978.0303 + 313.0035\,T$	(45) [a]	15
$1000 \le T \le 1500$, $\Delta_f G^\circ = -1688989.7482 + 328.1463\,T$	(46) [a]	15
$1500 \le T \le 2100$, $\Delta_f G^\circ = -1678617.5043 + 321.2909\,T$	(47) [a]	15
$933 \le T \le 1800$, $\Delta_f G^\circ = -1676000 + 320\,T$	(48)	16
$933 \le T \le 2100$, $\Delta_f G = -1677123 + 321.72\,T$	(49)	17
Al_4C_3		
$1000 \le T \le 1800$, $\Delta_f G = -233048.80 + 45.1872\,T$	(50)	14
$298 \le T \le 900$, $\Delta_f G^\circ = -216261.9943 + 42.8561\,T$	(51) [a]	15
$1000 \le T \le 1500$, $\Delta_f G^\circ = -263934.8888 + 94.1962\,T$	(52) [a]	15
$1500 \le T \le 2100$, $\Delta_f G^\circ = -265655.0109 + 95.3578\,T$	(53) [a]	15
$933 \le T \le 2100$, $\Delta_f G = -268000 + 103.6\,T$	(54)	17
Al_4O_4C		
$933 \le T \le 2100$, $\Delta_f G = -2333307 + 463.214\,T$	(55)	17

[a] From discrete values (see Table A.5).

Table 5
Other existing functions for enthalpies and entropies of formation of solid compounds in the Al–C–O system, in SI units (J, mole, K)

		References
Al_2O_3		
$298 \le T \le 933$, $\Delta_f H = -1676989.04 + 7.232\,T$	(56)	14
$298 \le T \le 933$, $\Delta_f S = -359.45375 + 7.232\,\ln T$	(57)	14
$933 \le T \le 1800$, $\Delta_f H = -1697699.84 + 6.81408\,T$	(58)	14
$933 \le T \le 1800$, $\Delta_f S = -379.03442 + 6.81408\,\ln T$	(59)	14
$1000 \le T \le 1500$, $\Delta_f H^\circ = -1708924.5158 + 16.2303\,T$	(60) [a]	15
$1500 \le T \le 2100$, $\Delta_f H^\circ = -1716624.6697 + 21.3533\,T$	(61) [a]	15
Al_4C_3		
$1000 \le T \le 1500$, $\Delta_f H^\circ = -258362.797 - 4.4757\,T$	(62) [a]	15
$1500 \le T \le 2100$, $\Delta_f H^\circ = -262521.4937 - 1.7304\,T$	(63) [a]	15

[a] From discrete values (see Table A.5).

Table 6
Comparison of Gibbs free energies, enthalpies and entropies of formation of solid compounds in the C–Al–O system

Equations compared	Intervals of relative errors (%)	
Janaf–(1); Janaf–(2); Janaf–(10)	Abs. R.E. < 0.1	[−0.0371; −0.0302]; [−0.0285; +0.0411]; [−0.0313; −0.0640]
(43)–(1); (48)–(3); (49)–(3); (56)–(10); (58)–(11); (58)–(12)	Abs. R.E. < 0.2	[−0.1563; −0.1965]; [−0.0411; +0.1242]; [−0.1632; −0.0047]; [−0.0605; −0.1803]; [−0.1721; −0.0213]; [−0.0213; +0.1224]
(44)–(2); Janaf–(3); Janaf–(11)	Abs. R.E. < 0.3	[−0.1845; −0.2359]; [+0.0411; +0.2637]; [+0.0686; −0.2042]
(44)–(3); (55)–(8)	Abs. R.E. < 0.4	[−0.2359; −0.3230]; [−0.3321; −0.2568]
(48)–(2); (49)–(2); Janaf–(12); (59)–(20)	Abs. R.E. < 0.5	[−0.4564; −0.0411]; [−0.4915; −0.1632]; [−0.2042; −0.4133]; [−0.1170; +0.4974]
(55)–(7); (59)–(21)	Abs. R.E. < 1	[−0.6022; −0.3321]; [+0.4974; +0.9468]
Janaf–(4); (54)–(5); Janaf–(13); Janaf–(14); (57)–(19)	Abs. R.E. < 4.5	[−0.2994; +3.4758]; [+1.0598; −4.3307]; [−2.5552; −0.3318]; [+0.0396; +2.8664]; [+1.5368; −0.1031]
(50)–(5); Janaf–(5)	Abs. R.E. > 4.5	[+13.3129; +45.7238]; [+4.0182; +19.5089]

Al_2O_3, all Gibbs free energies and enthalpies of formation are in agreement within 0.5% absolute relative error, and this abs. relative error does not exceed 1.54% for the entropy of formation. With Al_4O_4C only one reference is available for comparison, but the abs. relative error in free energies of formation is smaller than 1%. In contrast, the various equations suggested as Gibbs free energies of formation of Al_4C_3 are presented in Fig. 3. While there is a fair agreement between Eq. (54) and this study in the entire temperature interval 933–2100 K, although the relative error exceeds −4.33% at 2100 K, the discrepancy with

Table 7
Room temperature values of thermochemical functions for the solid compounds in the C–Al–O system, in SI units

	$\Delta_f G^\circ$	$\Delta_f H^\circ$	$\Delta_f S^\circ$	S°	References
Al_2O_3	Not mentioned	Not mentioned	Not mentioned	50.95	13
	−1579995	−1673600 ± 6275	−318.25	51.05 ± 0.40	14
	−1581878.35	−1675273.6	−313.4069	50.936	15
	m.d.	−1674000	m.d.	50.60	16
	−1582464.93132	−1675846.68502	−313.361589598	50.830460402	Present
Al_4C_3	−118830 ± 33470	−150200 ± 33470	−105.2685	101.90	13
	m.d.	−195393 ± 41850	m.d.	131 ± 10.5	14
	−203350.768	−215685.2	−41.3907	88.97	15
	−203959.516247	−221196.315368	−57.8416077886	72.5026922114	Present
Al_4O_4C	−2140953 ± 33470	−2272330 ± 33470	−440.8631	101.90	13
	−2189428.06056	−2320352.60684	−439.344115035	89.693384965	Present
Al_2OC	−664837.6 ± 41840	−717137.6 ± 41840	−175.5034	27.196	13
	Unstable below 1983.05 K				8,10–12, Present

Table 8
Other existing functions for the heat capacities of base components and solid compounds in the C–Al–O system, in SI units (J, mole, K)

			References
C (graphite)			
$298 \le T \le 2100$	$C_p = 17.155 + 4.2677 \times 10^{-3}\,T - 0.87864 \times 10^6/T^2$	(64)	14
	$C_p = 17.2 + 4.27 \times 10^{-3}\,T - 0.879 \times 10^6/T^2$	(65)	16
Al (solid)			
$298 \le T \le 933$	$C_p = 20.67 + 12.3846 \times 10^{-3}\,T$	(66)	14
	$C_p = 20.7 + 12.4 \times 10^{-3}\,T$	(67)	16
O_2 (g)			
$298 \le T \le 2100$	$C_p = 29.96 + 4.184 \times 10^{-3}\,T - 0.16736\ 10^6/T^2$	(68)	14
	$C_p = 30 + 4.18 \times 10^{-3}\,T - 1.7 \times 10^5/T^2$	(69)	16
Al_2O_3			
$298 \le T \le 2100$	$C_p = 115.02 + 11.7989 \times 10^{-3}\,T - 3.506192 \times 10^6/T^2$	(70)	13
$298 \le T \le 1800$	$C_p = 114.56 + 12.8867 \times 10^{-3}\,T - 3.430880 \times 10^6/T^2$	(71)	14
$298 \le T \le 900$	$C_p = 103.76 + 26.4429 \times 10^{-3}\,T - 2.903696 \times 10^6/T^2$	(72) [a]	15
$1000 \le T \le 1500$	$C_p = 113.11 + 12.9905 \times 10^{-3}\,T - 1.242119 \times 10^6/T^2$	(73) [a]	15
$1500 \le T \le 2100$	$C_p = 127.32 + 6.6605 \times 10^{-3}\,T - 10.947147 \times 10^6/T^2$	(74) [a]	15
$298 \le T \le 1800$	$C_p = 106.6 + 17.8 \times 10^{-3}\,T - 2.85 \times 10^6/T^2$	(75)	16
Al_4C_3			
$298 \le T \le 2100$	$C_p = 185.35 + 13.3470 \times 10^{-3}\,T - 5.183976 \times 10^6/T_2$	(76)	13
$298 \le T \le 600$	$C_p = 100.75 + 132.2144 \times 10^{-3}\,T$	(77)	14
$298 \le T \le 900$	$C_p = 154.3 + 30.36 \times 10^{-3}\,T - 4.3146 \times 10^6/T^2$	(78) [a]	15
$1000 \le T \le 1500$	$C_p = 179.20 + 6.8332 \times 10^{-3}\,T - 9.833936 \times 10^6/T^2$	(79) [a]	15
$1500 \le T \le 2100$	$C_p = 189.20 + 2.4711 \times 10^{-3}\,T - 17.333857 \times 10^6/T^2$	(80) [a]	15
Al_4O_4C			
$298 \le T \le 2100$	$C_p = 215.14 + 20.1669 \times 10^{-3}\,T - 6.401520 \times 10^6/T^2$	(81)	13
Al_2OC			
$298 \le T \le 2100$	$C_p = 100.12 + 8.3680 \times 10^{-3}\,T - 2.895328 \times 10^6/T^2$	(82)	13

[a] From discrete values (see Table A.5).

functions 51 through 53, soon appears following an almost perfect agreement at room temperature, and keeps increasing as the temperature increases. As to Eq. (50), it is clearly far remote towards too negative values.

The same trends appear in Table 7 which gives the room temperature values, at 298 K, of the thermochemical functions discussed so far, as well as the entropy values of solid compounds. Ref. 13, which was the first and most ancient to include

Table 9
Comparison of heat capacities of base components and solid compounds in the Al–C–O system

Equations compared	Intervals of relative errors (%)	
Janaf–(31); Janaf–(32); Janaf–(33)	Abs. R.E. < 0.1	[−0.0466; +0.0508]; [+0.0643; −0.0683]; [−0.0818; +0.0743]
(81)–(40); (81)–(41)	Abs. R.E. < 0.5	[+0.3279; −0.3202]; [−0.3649; −0.0919]
(71)–(34); (71)–(35); Janaf–(35); (81)–(39)	Abs. R.E. < 1.0	[+0.8688; −0.4878]; [−0.6104; +0.0168]; [+0.2150; −0.6533]; [−0.8958; +0.9187]
Janaf–(29); (70)–(34); (70)–(35); (70)–(36); (71)–(36); Janaf–(34); Janaf–(36)	Abs. R.E. < 1.5	[−1.3949; +1.4339]; [+0.4314; −1.0161]; [−1.2381; −0.9019]; [−0.9017; +1.2673]; [+0.0169; +1.1454]; [−1.2984; +0.6300]; [−0.0339; +1.2601]
(68)–(31); (69)–(31); (69)–(32); (69)–(33); (75)–(36)	Abs. R.E. < 2.5	[+1.6087; −2.4566]; [+1.6786; −2.3556]; [−2.4885; −1.0785]; [−1.0796; +1.9625]; [−0.2345; +1.9084]
Janaf–(28); (66)–(29); (67)–(29); (68)–(32); (68)–(33); (75)–(34); (75)–(35); (76)–(38)	Abs. R.E. < 5.0	[+1.1006; −2.5860]; [−0.7724; −4.4853]; [−0.6318; −4.3416]; [−2.5890; −1.1703]; [−1.1714; +2.6330]; [+0.7095; −2.7761]; [−2.8341; −0.2345]; [+3.9619; −3.6075]
(64)–(28); (65)–(28); (76)–(37); (77)–(37); Janaf–(37)	Abs. R.E. < 15.0	[+12.0672; −5.0801]; [−4.8495; +12.3711]; [+6.1857; +3.9615]; [+12.0445; +2.8780]; [−7.2147; −5.5130]
Janaf–(38); (82)–(42)	Abs. R.E. > 15.0	[−5.5591; −15.3317]; [−20.4471; −20.6747]

Table 10
Carbon monoxide partial pressures (atm) at equilibrium in some carbothermal reactions

Reaction	p_{CO} experimental (Ref. 13)	p_{CO} calculated (present study)
$2Al_2O_3 + 3C = Al_4O_4C + 2CO_{(g)}$ (a)	2.24×10^{-2} (1820 K) → 0.4803 (2100 K)	0.7347×10^{-2} (1820 K) → 0.238125 (2100 K)
$Al_2O_3 + 3C = Al_2OC + 2CO_{(g)}$ (b)	4.21×10^{-2} (1720 K) → 0.5263 (2030 K)	4.8714×10^{-2} (1983.05 K) → 0.087448 (2030 K)
$Al_4O_4C + 6C = Al_4C_3 + 4CO_{(g)}$ (c)	3.29×10^{-2} (1920 K) → 0.4079 (2100 K)	1.6973×10^{-2} (1920 K) → 0.147823 (2100 K)
$Al_4O_4C + Al_4C_3 = 8Al_{(l)} + 4CO_{(g)}$ (d)	1.10×10^{-2} (1920 K) → 0.2524 (2200 K)	0.1868×10^{-2} (1920 K) → 3.2882×10^{-2} (2100 K) (0.132105_5 at 2200 K)

Table 11
Measured high temperature Al equilibrium vapour pressure, vs. Al equilibrium saturated vapour pressure

Temperature (K)	P (mmHg)	
	Measured[13]	Sat. vapour pressure[20]
1902	13	2
2000	45	5
2080	125	10
2167	299	20

thermodynamic data on the Al_2O_3–Al_4C_3 system, is extremely misleading on Al_4C_3, especially for $\Delta_f G^\circ$ and $\Delta_f S^\circ$ and to a minor extent $\Delta_f H^\circ$; as to the room temperature entropy value of this compound, both Refs. 13 and 14 are problematic. In order to determine S° knowing $\Delta_f S^\circ$, the following well accepted base component values were used (J mol^{-1} K^{-1}): S°_{298} ($C_{(s)}$) = 5.6861; S°_{298} ($Al_{(s)}$) = 28.3215; S°_{298} ($O_{2(g)}$) = 205.0327.

Some other existing functions for heat capacities of base components and solid compounds in the Al–C–O system, are listed in Table 8 and compared with equations of this study, in Table 9. Here again, those with abs. relative errors larger than 10% pertain to aluminium carbide (Refs. 14 and 15) and aluminium oxycarbide Al_2OC (Ref. 13) as well as, more surprisingly, to graphite (Refs. 14 and 16). In all other cases, it can be seen that there is a reasonable agreement.

At this point it is timely to address the high temperature affinity of the solids discussed so far, for graphite, and to investigate the equilibrium pressure of some reactions at various temperatures between 1500 and 2100 K. For this purpose the linear expressions of Table A.3 are used, as well as $\Delta_f G^\circ$ ($CO_{(g)}$) = −117172.0234 − 84.4077 T, within less than 0.5% abs. relative error with Refs. 14–16. Table 10 mentions four of such reactions, labelled (a) through (d), and reports measured[13] equilibrium vapour pressures of carbon monoxide. In the same table, comparison with values calculated from the present study shows that the measured values are unquestionably higher. That they are in fact much too high is best seen when one compares (Table 11) the equilibrium vapour pressure of liquid aluminium as reported in Ref. 13, with the Al saturated vapour pressure as determined from Ref. 20. It then becomes clear that the measured vapour pressures are erroneous, as well as the heats and free energies of formation for Al_2OC, Al_4O_4C and Al_4C_3 reported in Ref. 13, since these were all calculated from pressure measurements.

5. Conclusion

A consistent set of thermochemical functions, including Gibbs free energies of formation, enthalpies and entropies of reactions, and heat capacities, are proposed for the base components and solid compounds in the C–Al–O system. The paper points out important discrepancies existing for aluminium carbide and aluminium oxycarbide Al_2OC, and suggests new equations to define these compounds more properly.

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Appendix A

The standard enthalpies and entropies of formation of Al oxide, carbide and oxycarbides, as obtained from Table 1 using Gibbs–Helmholtz equation, are listed in Tables A.1 and A.2 below. Table A.3 shows that Gibbs free energies of formation of Al_2O_3, Al_4C_3, Al_4O_4C and Al_2OC vary with temperature essentially like linear functions, confirming Ûlich approximation of nearly temperature-independent enthalpies (the constant terms of linear estimates) and entropies (minus the temperature coefficients of linear estimates) of reaction. It is of course an approximation, as shown by the variations of these quantities with temperature, also themselves almost perfectly linear in the various temperature ranges. Table A.4, which compares the 'constant' values of $\Delta_f H^\circ$ and $\Delta_f S^\circ$ with the actual values of Tables A.1 and A.2, gives the exactness of Ülich approximation.

Discrete data from Ref. 15 could, in most cases, be modelled according to classical functions, and Table A.5 shows that the relative errors with actual values are small.

Table A.1
Standard enthalpies of formation of solid compounds in the C–Al–O system, in SI units (J, mole, K)

Al_2O_3

$298 \le T \le 933$

$$\Delta_f H^\circ = -1692098.49628 + 20.79\,T + 1087.525 \times 10^{-6}\,T^2 - 5822.419 \times 10^{-9}\,T^3 + 3013.94125 \times 10^3/T \quad (10)$$

$933 \le T \le 1500$

$$\Delta_f H^\circ = -1703587.779 + 2320.216 \times 10^{-3}\,T + 5438.306 \times 10^{-6}\,T^2 - 516.378 \times 10^{-9}\,T^3 + 2663.970 \times 10^3/T \quad (11)$$

$1500 \le T \le 2100$

$$\Delta_f H^\circ = -1750864.909 + 42120.216 \times 10^{-3}\,T - 8878.444 \times 10^{-6}\,T^2 + 1299.49 \times 10^{-9}\,T^3 + 23155.87 \times 10^3/T \quad (12)$$

Al_4C_3

$298 \le T \le 933$

$$\Delta_f H^\circ = -198954.518109 - 19.20\,T + 26031.6 \times 10^{-6}\,T^2 - (58892.084/3) \times 10^{-9}\,T^3 - 11817.764 \times 10^3/T + 2378.7 \times 10^6/T^2 - 144 \times 10^9/T^3 \quad (13)$$

$933 \le T \le 2100$

$$\Delta_f H^\circ = -209944.693 - 51158.268 \times 10^{-3}\,T + 15316.705 \times 10^{-6}\,T^2 - 0.7266 \times 10^{-9}\,T^3 - 19102.964 \times 10^3/T + 2378.7 \times 10^6/T^2 - 144 \times 10^9/T^3 \quad (14)$$

Al_4O_4C

$298 \le T \le 933$

$$\Delta_f H^\circ = -2334566.14257 + 22.98\,T + 10800.5 \times 10^{-6}\,T^2 - (46383.604/3) \times 10^{-9}\,T^3 - 89.195 \times 10^3/T + 792.9 \times 10^6/T^2 - 48 \times 10^9/T^3 \quad (15)$$

$933 \le T \le 1500$

$$\Delta_f H^\circ = -2352531.936 - 13959.135 \times 10^{-3}\,T + 12356.643 \times 10^{-6}T^2 - 688.74 \times 10^{-9}\,T^3 - 2815.694666 \times 10^3/T + 792.9 \times 10^6/T^2 - 48 \times 10^9/T^3 \quad (16)$$

$1500 \le T \le 2100$

$$\Delta_f G^\circ = -2415568.109 + 39107.532 \times 10^{-3}\,T - 6732.357 \times 10^{-6}\,T^2 + 1732.4112 \times 10^{-9}T^3 + 24506.83868 \times 10^3/T + 792.9 \times 10^6/T^2 - 48 \times 10^9/T^3 \quad (17)$$

Al_2OC

$1983.05 \le T \le 2100$

$$\Delta_f H^\circ = -667653.2006 + 19187.316 \times 10^{-3}\,T + 2146.087 \times 10^{-6}\,T^2 + 432.9212 \times 10^{-9}\,T^3 + 1350.968668 \times 10^3/T + 792.9 \times 10^6/T^2 - 48 \times 10^9/T^3 \quad (18)$$

Table A.2
Standard entropies of formation of solid compounds in the C–Al–O system, in SI units (J, mole, K)

Al_2O_3

$298 \le T \le 933$

$$\Delta_f S^\circ = -448.646372462 + 20.79 \ln T + 2.17505 \times 10^{-3}\,T - 8.7336285 \times 10^{-6}\,T^2 + 1.506970625 \times 10^6/T^2 \quad (19)$$

$933 \le T \le 1500$

$$\Delta_f S^\circ = -359.696357 + 2.320216 \ln T + 10.876612 \times 10^{-3}\,T - 0.774567 \times 10^{-6}\,T^2 + 1.331985 \times 10^6/T^2 \quad (20)$$

$1500 \le T \le 2100$

$$\Delta_f S^\circ = -618.494584 + 42.120216 \ln T - 17.756888 \times 10^{-3}\,T + 1.949235 \times 10^{-6}\,T^2 + 11.577935 \times 10^6/T^2 \quad (21)$$

Al_4C_3

$298 \le T \le 933$

$$\Delta_f S^\circ = 58.9522033574 - 19.20 \ln T + 52.0632 \times 10^{-3}\,T - 29.446042 \times 10^{-6}\,T^2 - 5.908882 \times 10^6/T^2 + 1.5858 \times 10^9/T^3 - 0.108 \times 10^{12}/T^4 \quad (22)$$

$933 \le T \le 2100$

$$\Delta_f S^\circ = 231.026744 - 51.158268 \ln T + 30.633410 \times 10^{-3}\,T - 1.0899 \times 10^{-9}\,T^2 - 9.551482 \times 10^6/T^2 + 1.5858 \times 10^9/T^3 - 0.108 \times 10^{12}/T^4 \quad (23)$$

Al_4O_4C

$298 \le T \le 933$

$$\Delta_f S^\circ = -589.548342841 + 22.98 \ln T + 21.601 \times 10^{-3}\,T - 23.191802 \times 10^{-6}\,T^2 - 0.0445975 \times 10^6/T^2 + 0.5286 \times 10^9/T^3 - 0.036 \times 10^{12}/T^4 \quad (24)$$

$933 \le T \le 1500$

$$\Delta_f S^\circ = -402.586234 - 13.959135 \ln T + 24.713286 \times 10^{-3}\,T - 1.03311 \times 10^{-6}\,T^2 - 1.407847333 \times 10^6/T^2 + 0.5286 \times 10^9/T^3 - 0.036 \times 10^{12}/T^4 \quad (25)$$

$1500 \le T \le 2100$

$$\Delta_f S^\circ = -747.650536 + 39.107532 \ln T - 13.464714 \times 10^{-3}\,T + 2.5986168 \times 10^{-6}\,T^2 + 12.25341934 \times 10^6/T^2 + 0.5286 \times 10^9/T^3 - 0.036 \times 10^{12}/T^4 \quad (26)$$

Al_2OC

$1983.05 \le T \le 2100$

$$\Delta_f S^\circ = -281.192748 + 19.187316 \ln T + 4.292174 \times 10^{-3}\,T + 0.6493818 \times 10^{-6}\,T^2 + 0.675484334 \times 10^6/T^2 + 0.5286 \times 10^9/T^3 - 0.036 \times 10^{12}/T^4 \quad (27)$$

Table A.3
Linear expressions of standard thermochemical functions of Tables 1, A.1 and A.2, in SI units (J, mole, K)

		Reliability coefficient	Interval of relative error (10^{-2}%)
Al_2O_3			
$298 \le T \le 933$	$\Delta_f G^\circ = -1675594.0832 + 313.1813T$	1.0000	[−1.37; +2.39]
$933 \le T \le 1500$	$\Delta_f G^\circ = -1691664.2525 + 330.2555T$	1.0000	[−1.36; +1.76]
	$\Delta_f H^\circ = -1705024.4343 + 11.3094T$	0.9974	[+1.13; −1.32]
	$\Delta_f S^\circ = -341.5392 + 0.0093T$	1.0000	[−1.09; +0.33]
$1500 \le T \le 2100$	$\Delta_f G^\circ = -1683596.3293 + 324.8824T$	1.0000	[−1.58; +2.14]
	$\Delta_f H^\circ = -1711318.0314 + 15.5746T$	0.9997	[−0.70; +0.53]
	$\Delta_f S^\circ = -340.5310 + 0.0087T$	0.9997	[−0.52; +2.94]
Al_4C_3			
$298 \le T \le 933$	$\Delta_f G^\circ = -219728.7859 + 53.8955T$	0.9999	[+14.3; −10.63]
$933 \le T \le 1500$	$\Delta_f G^\circ = -263439.3224 + 100.5843T$	1.0000	[+ 3.88; −4.53]
$1500 \le T \le 2100$	$\Delta_f G^\circ = -262173.9443 + 99.8502T$	1.0000	[−12.95;+25.82]
Al_4O_4C			
$298 \le T \le 933$	$\Delta_f G^\circ = -2318737.7401 + 435.7241T$	1.0000	[+2.45; −2.14]
$933 \le T \le 1500$	$\Delta_f G^\circ = -2354465.4194 + 473.8687T$	1.0000	[−1.22; +1.61]
	$\Delta_f H^\circ = -2371004.8863 + 14.0389T$	0.9945	[+1.47; −1.77]
	$\Delta_f S^\circ = -487.7358 + 0.0115T$	0.9992	[−2.22; +3.01]
$1500 \le T \le 2100$	$\Delta_f G^\circ = -2343286.1443 + 466.4599T$	1.0000	[−1.77; +2.43]
	$\Delta_f H^\circ = -2385491.1627 + 23.7619T$	0.9988	[+1.34; −1.49]
	$\Delta_f S^\circ = -490.2696 + 0.0132T$	1.0000	[−0.84; −1.67]
Al_2OC			
$1983.05 \le T \le 2100$	$\Delta_f G^\circ = -615041.7130 + 123.2766T$	1.0000	[−0.37; +0.41]
	$\Delta_f H^\circ = -682074.8196 + 32.8558T$	1.0000	[+0.14; −0.25]
	$\Delta_f S^\circ = -156.1373 + 0.0161T$	1.0000	[−0.20; +0.21]

Table A.4
Exactness of Ülich approximation (%)

Temperature interval (K)	Al_2O_3 $\Delta_f H^\circ$; $\Delta_f S^\circ$	Al_4C_3 $\Delta_f H^\circ$; $\Delta_f S^\circ$	Al_4O_4C $\Delta_f H^\circ$; $\Delta_f S^\circ$	Al_2OC $\Delta_f H^\circ$; $\Delta_f S^\circ$
298–933	+0.0508, −0.1397; +0.6422, −0.9143	+0.6687, −0.4143; +7.3328, −2.2263	+0.0878, −0.1386; +1.1357, −0.8813	
933–1500	+0.1530, −0.2262; +0.7783, −0.8150	−0.4468, +0.2249; −1.1807, +0.4278	+0.1299, −0.2095; +0.6397, −0.7313	
1500–2100	+0.2519, −0.3024; +0.8254, −0.7777	+0.6747, −1.4357; +1.1054, −1.8599	+0.2665, −0.3432; +0.8454, −0.8549	
1983.05–2100				+0.3040, −0.3208; +0.7593, −0.7679

Table A.5
Comparison of discrete Janaf data with a number of equations

Equations	Intervals of relative errors (%)	
(45), (46), (47), (53), (60), (61), (62), (63), (79)	Abs. R.E. $< 5.10^{-2}$	[−1.55; +1.96]; [−1.48; +1.78]; [−2.15; +2.98]; [+4.04; −3.74]; [+1.02; −1.07]; [−1.16; +0.90]; [+3.08; −3.12]; [−4.66; +3.69]; [−3.40; +1.09][a]
(31), (32), (33), (51), (52), (73), (74), (80)	Abs. R.E. $< 32.1 \times 10^{-2}$	[−4.79; +5.06]; [+7.06; −6.78]; [−8.68; +8.11]; [+8.6; −11.86]; [+4.29; − 5.05]; [−29.74; +32.08]; [−11.07; +12.04]; [−5.40; +8.92][a]
(29), (72), (78)	Abs. R.E. < 1.751	[−1.3940; +1.4339]; [+1.10; −0.90]; [+1.7316; −1.7509]

[a] All limits to be multiplied by 10^{-2}.

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