



# Heats of formation for aluminium compounds with EnAt1 and EnAt2

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## Abstract

Enthalpies of formation of twenty-nine compounds of aluminium were calculated employing various density functional theory (DFT) (B3LYP, B2PLYP, LC-wPBE, PBE1PBE, BMK, M06 and M06-2X) and composite methods (EnAt1, EnAt2, G3X-CEP, G3X(CCSD)-CEP and G4), using atomization. The best agreement with experimental data was achieved by using Gn and Gn-CEP multilevel techniques. It was found that the best performance among DFT methods within the atomization approach demonstrated the long range corrected M06-2X level theory. The mean absolute error calculated for EnAt1 and EnAt2, which has recently been reported as a very accurate method for calculating enthalpies of formation, for 248 compounds from the G3/05 test set presented the best results when compared with functional DFT.

**Keywords** Aluminium compounds · EnAt1 · EnAt2 · Composite methods · Density functional theory

## 1 Introduction

Aluminium is the most common metal in the world and the second most used metal. It is constantly found associated with other atoms, such as chlorine [1], oxygen [2], hydrogen [3] and fluorine [4]. Aluminium reacts so quickly with oxygen that it is never naturally found in its pure form. Compounds of aluminium are found in large quantities in the Earth's crust as an ore called bauxite [5].

Aluminium is found with other metals in many different ways as composites (hybrid materials), such as aluminium matrix composites. Metal matrix composites (MMCs) [6] consist of metal alloys mounted with fibres, particulates or whiskers. Alloys of numerous metals (i.e. aluminium-titanium [7] and aluminium-copper [8]) have been used as matrices to date. In the NASA Space Shuttle [9], for example, many materials are produced from aluminium mounted with boron fibres [10].

Enthalpy of formation (298.15 K) of compounds of aluminium, calculated with composite methods, presented better results when compared with ab initio methods. Curtiss et al. [11, 12] calculated that  $\text{Al}_2\text{Cl}_6$  presented a mean absolute error (MAE) of 7.8 and 5.2 kcal mol<sup>-1</sup> for G3X and G4, respectively, whereas for the density functional theory with 6-311+G(3df,2p), the MAE was -29.1 kcal mol<sup>-1</sup>, -31.9 kcal mol<sup>-1</sup> and 30.0 kcal mol<sup>-1</sup> for B3LYP, O3LYP and VSXC [11], respectively.

A recent endeavour to reduce the CPU time of calculations suggested the Gn theory started by Pereira et al. [13, 14], which associates a compact effective potential (CEP) [15] with the G3 theory, resulting in a method known as G3CEP [13, 14]. After this first successful generalization by combining pseudopotential with the G3 theory, other proposals were expanded, such as G3(MP2)//B3LYP-CEP [16], G3(MP2)-CEP [17], G4-CEP [18], G3(MP2)//B3-SBK [19], G3X-CEP [20] and G3X(CCSD)-CEP [20]. Enforcement of these methods manifested a significant decrease in CPU time, preserving an outstanding accuracy when compared with the original all-electron versions. These methods were applied to transition metals [21] and pKa [22], for example.

Silva and Custodio [20] revealed the chance to improve the calculated enthalpies of formation with respect to accurate experimental data by scaling the atomization energies. This sequence of steps, along with the G3X and G3X(CCSD) methods and pseudopotential, generated EnAt1

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[20] and EnAt2 [20], which provided results as accurate as the combination of G4CEP [18] and G3CEP [13] theories.

For 248 enthalpies of formation from the G3/05 test set, the MAE of the calculations with EnAt1 (1.02 kcal mol<sup>-1</sup>) and EnAt2 (0.98 kcal mol<sup>-1</sup>) is significantly better than the G3X-CEP results (1.16 kcal mol<sup>-1</sup>) and G3X(CCSD)-CEP (1.12 kcal mol<sup>-1</sup>) with the original experimental atomization energies. Silva and Custodio [20] calculated that Al<sub>2</sub>Cl<sub>6</sub> presented a MAE of 6.7 and 7.6 kcal mol<sup>-1</sup> for G3X-CEP and G3X(CCSD)-CEP, respectively, whereas the MAE was 0.0 kcal mol<sup>-1</sup> for both EnAt1 and EnAt2 methods.

EnAt1 and EnAt2 had the scaling of the experimental atomization energies for the calculation of the enthalpies of formation. The experimental atomization energy of every element of the periodic table is multiplied by an adaptable parameter that decreases the MAE between the theoretical enthalpies of formation and the experimental one. Every parameter is set initially equal to 1.0 and optimized using the simplex method [23]. At the end of this optimization, it is complemented with the re-optimization of the higher-level correction (HLC) parameters.

In the present work, the thermochemical values of aluminium compounds considered have been determined using the EnAt1 and EnAt2 methods, which presented the best results.

## 2 Computational methods

Heats of formation at 298.15 K and 1 atm were computed from total atomization energies. This requires an accurate and balanced energetic description of the molecule and its constituent atoms, which places stringent requirements on the quantum methods employed.

The results obtained atomization using the density functional theory (DFT) with different exchange and correlation: B3LYP [24, 25], B2PLYP [26], BMK [27], M06 [28], M06-2X [28], LC-wPBE [29, 30] and PBE1PBE [29, 31]. The 6-311G(d,p) [32, 33], cc-pVDZ [34], cc-pVTZ [35], aug-cc-pVTZ [34, 35] basis sets were employed in the DFT calculation. Besides the optimized geometries at the B3LYP/6-311G(d,p) level, different strategies have been adopted by the composite methods, such as the following: (a) B3LYP/6-311G(d,p) was used for the geometry optimization and with a scaling factor of  $\lambda = 0.99$  for vibrational frequencies as used by B3LYP/cc-pVDZ, B3LYP/cc-pVTZ, B3LYP/extrapolation, B2PLYP/cc-pVDZ, B2PLYP/cc-pVTZ, B2PLYP/extrapolation, MP2/cc-pVDZ, MP2/cc-pVTZ, MP2/extrapolation, BMK/aug-cc-pVTZ, M06/aug-cc-pVTZ, M06-2x/aug-cc-pVTZ, LC-wPBE/aug-cc-pVTZ and PBE1PBE/aug-cc-pVTZ; (b) B3LYP/6-31G(2df,p) was used for geometry optimization and frequencies with  $\lambda = 0.9854$ , used by G3X-CEP, G3X(CCSD)-CEP, G4,

EnAt1 and EnAt2; (c) extrapolation is described in G4 theory [12].

In summary, we have adapted the G3X and G3X(CCSD) methods together with the CEP pseudopotential to create two methods labelled as: G3X-CEP and G3X(CCSD)-CEP [20]. The G3X reference energy is calculated at the QCISD(T)/6-31G(d) level, for as much as the G3X(CCSD) regards the CCSD(T)/6-31G(d) level of theory [20]. The general expression for G3X contains corrections for diffuse ( $\Delta E_+$ ) and polarization ( $\Delta E_{2df,p}$ ) functions, electron correlation effects ( $\Delta E_{QCISD(T)}$ ), effects from the size of the basis functions ( $\Delta E_{G3large}$ ), and improvement in the G3large basis set ( $\Delta E_{HF}$ ), spin-orbit correction ( $E_{SO}$ ) from the literature, zero point energy and thermal effects ( $E_{ZPE}$ ), and an empirical higher level correction ( $E_{HLC}$ ). The combination of all these effects is summarized in the following expression [20]:

$$E_{G3X} = E[MP4/6 - 31G(d)] + \Delta E_+ + \Delta E_{2df,p} + \Delta E_{QCISD(T)} + \Delta E_{G3large} + \Delta E_{HF} + E_{SO} + E_{ZPE} + E_{HLC} \quad (1)$$

where the mathematical definition of each correction is:

$$\begin{aligned} \Delta E_+ &= E[MP4/6 - 31 + G(d)] - E[MP4/6 - 31G(d)]; \\ \Delta E_{2df,p} &= E[MP4/6 - 31G(2df,p)] - E[MP4/6 - 31G(d)]; \\ \Delta E_{QCISD(T)} &= E[QCISD(T)/6 - 31G(d)] - E[MP4/6 - 31G(d)]; \\ \Delta E_{G3largeXP} &= E[MP2(full)/G3largeXP] \\ &\quad - E[MP2/6 - 31G(2df,p)] - E[MP2/6 - 31 + G(d)] \\ &\quad + E[MP2/6 - 31G(d)] \text{ and} \\ \Delta E_{HF} &= E[HF/G3Xlarge] - E[HF/G3large]. \end{aligned}$$

The molecular equilibrium geometries were obtained from B3LYP/6-31G(2df,p). The zero point energy (ZPE) is also obtained from the harmonic approximation at the B3LYP/6-31G(2df,p) level, and the frequencies are scaled by a factor of 0.9854 [20].

In this work, the behaviour of the composite techniques EnAt1 and EnAt2 is evaluated for a test set of enthalpies of formation of 29 representative molecules containing second-row and third-row periodic table elements. The main criteria for selecting these 29 molecules were an experimental uncertainty of less than 1 kcal mol<sup>-1</sup>. This test set also included six molecules with larger uncertainties.

All calculations were performed by using the Gaussian 09 package of programs [36].

## 3 Results and discussion

Table 1 shows the enthalpy of formation (298.15 K) for compounds of aluminium, calculated using G3X-CEP, G3X(CCSD)-CEP, G4, EnAt1 and EnAt2 and compared to experimental data. The resulting MAE, standard deviation

**Table 1** Experimental and theoretical enthalpies of formation ( $\text{kcal mol}^{-1}$ ) for the aluminium compounds. G3X-CEP, G3X(CCSD)-CEP, G4, EnAt1 and EnAt2 are the differences between the experimental data and the G3X-CEP, G3X(CCSD)-CEP, G4, EnAt1 and EnAt2 calculations, respectively

Substance	G3X-CEP	G3X(CCSD)-CEP	G4	EnAt1	EnAt2	Exp. <sup>a</sup>
$\text{AlF}_4^-$	7.23	7.40	3.51	1.78	2.43	$-463.4 \pm 2.4$
$\text{AlClF}_2$	4.82	4.85	1.35	0.28	0.65	-238.8
$\text{AlH}$	4.17	4.2	3.9	-0.64	-0.29	62
$\text{AlH}_4^-$	3.2	3.22	1.18	-1.93	-1.66	-9.49
$\text{AlO}$	6.32	4.72	4.71	1.25	-0.09	21.79
$\text{AlClF}_2$	4.1	4.34	1.6	0.12	0.29	-189
$\text{AlCl}$	2.34	2.49	2.74	-2.1	-1.78	-12.30
$\text{Al}_2\text{F}_6$	9.52	9.61	2.45	-0.44	0.5	-628.1
$\text{AlBr}$	2.02	2.17	3.11	-2.51	-2.06	3.8
$\text{AlBr}_3$	1.15	1.53	2.02	-2.76	-2.16	-98.1
$\text{Al}_2\text{O}$	8.23	8.12	7.94	0.39	1.08	-31.07
$\text{AlS}$	10.95	10.35	9.4	5.42	5.3	57
$\text{AlBO}_2$	-1.81	-2.14	-2.72	-7.11	-5.74	-129.4
$\text{NaAlF}_4$	0.09	0.19	-4.58	-6.01	-5.63	-446.7
$\text{AlHO}$	1.43	1.41	2.11	-3.63	-3.21	-43
$\text{AlO}_2^-$	9.2	8.01	4.16	3.44	2.86	$-107 \pm 30$
$\text{AlClF}_3$	6.63	6.88	3.14	1.63	2.15	$-415.87 \pm 8$
$\text{AlCl}_2\text{F}_2^-$	5.96	6.3	2.96	1.4	1.82	$-367.5 \pm 3.1$
$\text{Al}_2\text{H}_7^-$	6.62	6.66	4.35	-3.25	-2.7	-14.8
$\text{Al}_3$	16.48	16.04	-5.86	1.55	2.13	116.13
$\text{C}_3\text{H}_9\text{Al}$	1.9	1.85	1.08	-3.18	-2.64	$-13.6 \pm 2.3$
$\text{Al}_2\text{S}$	2.49	2.25	0.19	-8.69	-7.99	$34.3 \pm 4.9$
$\text{Al}_2\text{O}_2$	-7.16	-3.04	-10.21	-11.5	-12.42	-94.3
$\text{C}_6\text{H}_{15}\text{Al}$	-7.44	-7.52	-9.06	-12.86	-12.02	$-23.9 \pm 1.2$
$\text{AlF}$	2.62	2.62	2.26	-2.27	-1.9	-63.5
$\text{AlC}$	-4.98	-5.05	-4.71	-8.93	-8.85	164.8
$\text{Al}_2\text{Cl}_6$	6.70	7.6	-2.96	0.0	0.0	-309.7
$\text{AlF}_3$	4.90	5.1	-3.37	0.0	-0.7	-289
$\text{AlCl}_3$	2.20	2.6	0.1	-2.2	-1.9	-139.7
MAE <sup>b</sup>	3.79	3.58	3.47	3.23	3.09	
Std <sup>c</sup>	5.14	4.80	4.54	4.32	4.25	
Lar. neg. dev. <sup>d</sup>	-7.44	-7.52	-10.21	-12.86	-12.42	
Lar. pos. dev. <sup>e</sup>	16.48	16.04	9.4	5.42	5.3	

<sup>a</sup>Data from [40] (298.15 K, 1 atm)<sup>b</sup>MAE is the mean absolute error<sup>c</sup>SD is the standard deviation<sup>d</sup>Lar. neg. dev. is largest negative deviation<sup>e</sup>Lar. pos. dev. is largest positive deviation

(Std. Dev.), largest negative deviation (lar. neg. dev) and largest positive deviation (lar. pos. dev.) are also reported in Table 1. Comparing the MAEs, EnAt1 and EnAt2 result in MAEs of 3.23 and 3.09  $\text{kcal mol}^{-1}$ , respectively, while G3X-CEP, G3X(CCSD)-CEP and G4 result in MAEs of 3.79, 3.58 and 3.47  $\text{kcal mol}^{-1}$ , respectively. The difference between the general performance of calculations with EnAt2 and G4 is 0.38  $\text{kcal mol}^{-1}$ .

The largest positive deviation for G4, EnAt1 and EnAt2 is for  $\text{AlS}$ , with a deviation of 9.4, 5.42 and 5.3  $\text{kcal mol}^{-1}$ , respectively (see Table 1), while the largest

negative deviation for G3X-CEP and G3X(CCSD)-CEP is for  $\text{C}_6\text{H}_{15}\text{Al}$ , with a deviation of -7.44 and -7.52  $\text{kcal mol}^{-1}$ , respectively (see Table 1). A total of 21% of the enthalpies of formation calculated with G4 showed a deviation between  $\pm 2$   $\text{kcal mol}^{-1}$ . A greater percentage (44%) was obtained for the results calculated with EnAt1 and EnAt2. Calculations using G4 also resulted in only 48% of the deviations between  $\pm 3$   $\text{kcal mol}^{-1}$ , while 62% and 72% of the results were observed for EnAt1 and EnAt2, respectively.

Some results from the literature are calculated at an equivalent level and can be partially compared with those

obtained using the EnAt1 and EnAt2 calculations. Cobos [37] performed calculations of AlH at the B3LYP/6-311++G(d,p), B3LYP/6-311++G(3df,3pd) and B3LYP/6-311++G(3d2f,3pd), with a deviation of 2.1, 2.7 and 2.7 kcal mol<sup>-1</sup>, respectively, and EnAt1 and EnAt2 with a deviation of -0.64 and -0.29 kcal mol<sup>-1</sup>, respectively. These results of EnAt1 and EnAt2 offered significant increases in accuracy compared with B3LYP in a different basis set.

For most compounds, the MAE of EnAt1 and EnAt2 atomization-based estimates is lower than the corresponding G3X-CEP, G3X(CCSD)-CEP and G4 atomization-based estimates by 3.47–3.79 kcal mol<sup>-1</sup>. Estimates of the enthalpy of formation (298.15 K) value for AIS (lar. pos. dev.) from the EnAt1 and EnAt2 calculations deviated by 5.42 and 5.3 kcal mol<sup>-1</sup>, respectively. These values are still better than the PM6 and PM5 values calculated by Stewart [38], with a deviation of -5.9 and -13.0 kcal mol<sup>-1</sup>, respectively.

The following are heats of formation values (kcal mol<sup>-1</sup>) at 0 K for G3X-CEP, G3X(CCSD)-CEP, G4, B3LYP, B2PLYP, MP2, LC-wPBE, PBE1PBE, BMK, M06 and M06-2X: H (51.63 ± 0.001), B (136.2 ± 0.2), C (169.98 ± 0.1), O (58.99 ± 0.02), F (18.47 ± 0.007), Na (25.69 ± 0.17), Al (78.23 ± 1.00), S (65.66 ± 0.06) and Cl (28.59 ± 0.001). However, Silva and Custodio [20] proposed the possibility of refining the calculated enthalpies of formation with respect to accurate experimental data by scaling these values at 0 K to create EnAt1 and EnAt2. Heats of formation values (kcal mol<sup>-1</sup>) at 0 K for EnAt1 are: H (51.57), B (134.43), C (170.18), O (59.35), F (18.73), Na (26.73), Al (83.12), S (65.52) and Cl (28.41), and values at 0 K for EnAt2 are: H (51.61), B (135.08), C (170.01), O (59.17), F (18.60), Na (26.92), Al (82.76), S (66.12) and Cl (28.47).

Table 2 shows the enthalpy of formation (298.15 K) for compounds of aluminium calculated using B3LYP/6-311G(d,p), B3LYP/cc-pVDZ, B3LYP/cc-pVTZ, B3LYP/extrapolation, B2PLYP/cc-pVDZ, B2PLYP/cc-pVTZ, B2PLYP/extrapolation, MP2/cc-pVDZ, MP2/cc-pVTZ and MP2/extrapolation compared to experimental data. The lowest deviation from the experimental data was observed for aluminium compounds (29 compounds) with mean absolute error of 13.28 kcal mol<sup>-1</sup> for MP2/extrapolation, while the MAE for B3LYP/extrapolation and B2PLYP/extrapolation was 16.98 kcal mol<sup>-1</sup> and 19.94 kcal mol<sup>-1</sup>, respectively. Only 21% and 17% for the B3LYP/extrapolation and MP2/extrapolation calculations, respectively, show deviations between ± 2 kcal mol<sup>-1</sup>, whereas in B2PLYP/extrapolation, 3% of the results are between this limit. Most of the deviations are concentrated above ± 2 kcal mol<sup>-1</sup>.

We studied the behaviour of B2PLYP for a test set. This method shows a stronger basis set dependence than B3LYP and MP2. B2PLYP is for the cc-pVTZ basis set; the MAE reaches its smallest value at 20.54 kcal mol<sup>-1</sup>. When the

basis set is decreased to the cc-pVDZ level, the MAD becomes 30.44 kcal mol<sup>-1</sup>. Further tuning of the empirical parameters did not improve the B2PLYP results compared with B3LYP, even though some of the MP2 correlation is included in B2PLYP.

The accuracy of extrapolations can be compared among the calculations using the respective functionals and cc-pVDZ and cc-pVTZ basis sets. The best results were obtained using MP2/extrapolation, which yielded accuracy superior to the B3LYP/extrapolation and B2PLYP/extrapolation. Measuring the value of the energies with respect to the three functionals and the cc-pVDZ for cc-pVTZ basis sets, the errors were systematically reduced with the enlargement of the basis set. The typical performance of the extrapolation is compatible or better than the results obtained with the respective functionals and cc-pVDZ and cc-pVTZ basis sets.

Chinini and Custodio [39] calculated that Al<sub>2</sub>Cl<sub>6</sub> presented a MAE of -24.73 kcal mol<sup>-1</sup> for B3LYP/extrapolation using a different extrapolation formula (cc-pVDZ for cc-pVTZ basis sets) including corrections for electron number. In this situation, the MAE was -27.81 kcal mol<sup>-1</sup> for B3LYP/extrapolation.

We have also examined five density functional methods for the 29-molecule set. These results are given in Table 3. The density functional methods tested include: LC-wPBE, PBE1PBE, BMK, M06 and M06-2X. The results indicate that M06-2X performs the best with a MAD of 16.14 kcal mol<sup>-1</sup>. The PBE1PBE performed much worse, with MAD of 26.88 kcal mol<sup>-1</sup>. Density functional methods, such those in Table 3, performed much worse than the EnAt1 and EnAt2 methods for the 29 enthalpies. Thus, they are much less reliable than the EnAt1 and EnAt2 methods and are not recommended for use on compounds of aluminium.

The 29 enthalpies calculated and shown in Table 3 show a tendency towards larger dispersion of the results for M06-2X when compared to the EnAt1 and EnAt2 methods. The distribution indicates that 3% of the presented cases correspond to 1 molecule accuracy in the range of ± 2 kcal mol<sup>-1</sup> and 17% of the set test calculated with PBE1PBE showed a deviation between ± 2 kcal mol<sup>-1</sup>.

The discrepancy in the results is due to the molecules of C<sub>3</sub>H<sub>9</sub>Al and C<sub>6</sub>H<sub>15</sub>Al. The enthalpy of formation for compounds of aluminium without C<sub>3</sub>H<sub>9</sub>Al and C<sub>6</sub>H<sub>15</sub>Al presented results for MAE of LC-wPBE (8.30 kcal mol<sup>-1</sup>), PBE1PBE (15.96 kcal mol<sup>-1</sup>), BMK (14.68 kcal mol<sup>-1</sup>), M06 (13.61 kcal mol<sup>-1</sup>) and M06-2X (13.39 kcal mol<sup>-1</sup>), which are worse than MAE for EnAt1 (3.23 kcal mol<sup>-1</sup>) and EnAt2 (3.09 kcal mol<sup>-1</sup>) for C<sub>3</sub>H<sub>9</sub>Al and C<sub>6</sub>H<sub>15</sub>Al.

In agreement with the reported results of Curtiss et al. [11, 12], the VSXC/6-311 + G(3df,2p) and TPSS/6-311 + G(3df,2p) methods calculated deviations of 3.9 and -2.8 kcal mol<sup>-1</sup> for AlF, respectively. In this work,

**Table 2** Experimental and theoretical enthalpies of formation (kcal mol<sup>-1</sup>) for the aluminium compounds

Substance	B3LYP <sup>f</sup>	B3LYP <sup>g</sup>	B3LYP <sup>h</sup>	B3LYP <sup>i</sup>	B2PLYP <sup>g</sup>	B2PLYP <sup>h</sup>	B2PLYP <sup>i</sup>	MP2 <sup>g</sup>	MP2 <sup>h</sup>	MP2 <sup>i</sup>	Exp. <sup>a</sup>
AlF <sub>4</sub> <sup>-</sup>	-27.62	-37.23	-14.50	-8.96	-92.43	-68.22	-62.32	-43.62	-11.2	-3.28	-463.4 ± 2.4
AlClF <sub>2</sub>	-12.56	18.46	-3.26	0.45	-51.13	-33.38	-29.06	-19.62	2.22	7.55	-238.8
AlH	26.72	3.24	4.73	5.09	-3.05	-1.64	-1.30	1.37	3.71	4.28	62
AlH <sub>4</sub> <sup>-</sup>	14.09	7.53	14.18	15.80	-16.38	-10.01	-8.46	-1.40	8.75	11.22	-9.49
AlO	-1.31	-4.70	2.90	4.76	-32.32	-23.69	-21.59	-8.19	2.53	5.14	21.79
AlClF <sub>2</sub>	-18.62	-23.30	-10.85	-7.81	-48.34	-34.13	-30.67	-22.91	-4.80	-0.38	-189
AlCl	-3.60	-4.88	-1.82	-1.08	-13.45	-10.16	-9.36	-5.33	-0.43	0.77	-12.30
Al <sub>2</sub> F <sub>6</sub>	-40.39	-52.51	-25.55	-18.98	-131.3	-97.29	-89.90	-55.88	-13.3	-2.96	-628.1
AlBr	1.88	1.14	2.89	3.32	-6.78	-4.87	-4.41	0.9	4.50	5.37	3.8
AlBr <sub>3</sub>	-6.04	-8.86	-3.36	-2.02	-24.45	-18.35	-16.46	-5.95	4.62	7.19	-98.1
Al <sub>2</sub> O	-4.77	-10.26	-1.40	0.75	-36.65	-26.82	-24.43	-11.52	1.61	4.81	-31.07
AlS	4.65	2.74	6.25	7.11	-10.99	-7.26	-6.36	1.64	7.15	8.49	57
AlBO <sub>2</sub>	1.19	39.11	6.16	-1.87	-11.70	-41.85	-49.19	56.59	8.17	-3.63	-129.4
NaAlF <sub>4</sub>	-32.73	-38.14	-25.69	-22.66	-91.58	-75.38	-71.46	-41.52	-18.8	-13.27	-446.7
AlHO	-1.56	-6.30	2.47	4.60	-32.71	-23.39	-21.12	-9.97	2.66	5.73	-43
AlO <sub>2</sub> <sup>-</sup>	-15.39	-9.51	12.63	-0.71	-67.82	-44.15	-57.70	-13.84	15.63	4.09	-107 ± 30
AlClF <sub>3</sub>	-23.29	-34.28	-14.54	-9.73	-82.57	-61.43	-56.28	-39.46	-10.6	-3.51	-415.87 ± 8
AlCl <sub>2</sub> F <sub>2</sub> <sup>-</sup>	-20.42	-32.05	-15.07	-10.93	-162.16	-55.10	-29.02	-35.80	-10.25	-4.03	-367.5 ± 3.1
Al <sub>2</sub> H <sub>7</sub> <sup>-</sup>	26.07	16.55	27.14	29.73	-21.44	-11.03	-8.49	4.11	20.75	24.80	-14.8
Al <sub>3</sub>	-25.90	-28.14	-23.68	-22.59	-52.66	-48.56	-47.56	-26.72	-19.24	-17.42	116.13
C <sub>3</sub> H <sub>9</sub> Al	55.55	36.95	59.71	65.25	-43.51	-22.64	-17.55	41.13	55.69	63.75	-13.6 ± 2.3
Al <sub>2</sub> S	-16.71	-18.27	-32.67	-36.18	-35.61	-31.10	-30	-19.36	-11.85	-10.02	34.3 ± 4.9
Al <sub>2</sub> O <sub>2</sub>	-28.32	-36.28	-18.34	18.03	-96.18	-75.94	-71	-37.07	-10.68	-4.25	-94.3
C <sub>6</sub> H <sub>15</sub> Al	90.96	64.87	97.05	104.9	-81.34	-52.03	-44.88	41.13	91.67	104	-23.9 ± 1.2
AlF	-6.14	-7.55	-2.22	-0.93	-23.87	-17.59	-16.06	-9.41	-1.27	0.71	-63.5
AlC	-37.59	-39.72	-36.49	-35.70	-56.00	-52.86	-52.09	-45.62	-41.02	-39.90	164.8
Al <sub>2</sub> Cl <sub>6</sub>	-47.16	-52.91	-32.73	-27.81	-88.44	-66.63	-60.07	-46.02	-14.97	-7.41	-309.7
AlF <sub>3</sub>	-21.86	-29.14	-10.85	-6.40	-69.37	-47.79	-42.53	-31.65	-5.73	0.58	-289
AlCl <sub>3</sub>	18.53	-22.32	-12.09	-9.59	-39.64	-28.51	-25.80	-20.23	-5.28	-1.64	-139.7
MAE <sup>b</sup>	20.46	21.19	16.21	16.98	30.44	20.54	19.94	20.02	14.17	13.28	
Std <sup>c</sup>	29.07	27.71	23.02	28.99	38.62	24.65	24.25	26.85	23.79	25.90	
Lar. neg. dev. <sup>d</sup>	-47.16	-52.91	-36.49	-36.18	-162.16	-97.29	-89.90	-55.88	-41.02	-39.90	
Lar. pos. dev. <sup>e</sup>	90.96	64.87	97.05	104.8	-3.05	-1.64	-1.30	56.59	91.67	103.9	

B3LYP, B2PLYP and MP2 are the differences between the experimental data and the B3LYP, B2PLYP and MP2 calculations, respectively

<sup>a</sup>Data from [40] (298.15 K, 1 atm)

<sup>b</sup>MAE is the mean absolute error

<sup>c</sup>SD is the standard deviation

<sup>d</sup>Lar. neg. dev. is largest negative deviation

<sup>e</sup>Lar. pos. dev. is largest positive deviation

<sup>f</sup>Calculations using the 6-311G(d,p) basis set

<sup>g</sup>Calculations using the cc-pVDZ basis set

<sup>h</sup>Calculations using the cc-pVTZ basis set

<sup>i</sup>Calculations using a linear two-point extrapolation and Dunning's cc-pVnZ basis sets (cc-pVDZ and cc-pVTZ basis sets)

we found results corresponding to Curtiss for LC-wPBE (-2.13 kcal mol<sup>-1</sup>), PBE1PBE (-5.58 kcal mol<sup>-1</sup>), BMK (0.18 kcal mol<sup>-1</sup>), M06 (2.44 kcal mol<sup>-1</sup>) and M06-2X (2.25 kcal mol<sup>-1</sup>). Zhao and Truhlar [28] showed M06-2X

and M06 (these two hybrid meta-GGA exchange–correlation functionals) are the best functionals for thermochemistry calculations when compared to other functionals

**Table 3** Experimental and theoretical enthalpies of formation ( $\text{kcal mol}^{-1}$ ) for the aluminium compounds

Substance	LC-wPBE <sup>j</sup>	PBE1PBE <sup>j</sup>	BMK <sup>j</sup>	M06 <sup>j</sup>	M06-2X <sup>j</sup>	Exp. <sup>a</sup>
AlF <sub>4</sub> <sup>-</sup>	0.22	-19.29	-2.72	-1.95	2.84	-463.4 ± 2.4
AlClF <sub>2</sub>	6.09	-2.80	7.07	8.11	8.35	-238.8
AlH	0.81	0.73	4.07	7.53	5.16	62
AlH <sub>4</sub> <sup>-</sup>	11.06	4.43	8.64	14.03	8.61	-9.49
AlO	0.73	-0.57	2.04	2.46	2.96	21.79
AlClF <sub>2</sub>	-1.18	-5.37	3.53	3.45	2.96	-189
AlCl	-2.54	-0.16	4.41	5.36	5.09	-12.30
Al <sub>2</sub> F <sub>6</sub>	-4.57	-31.63	-7.91	-5.30	2.27	-628.1
AlBr	1.18	4.79	5.62	4.80	2.28	3.8
AlBr <sub>3</sub>	5.19	8.72	6.50	0.10	5.50	-98.1
Al <sub>2</sub> O	-1.37	-4.50	5.06	5.99	9.53	-31.07
AlS	4.06	9.24	12.67	11.44	11.65	57
AlBO <sub>2</sub>	7.09	3.24	18.96	15.40	16.13	-129.4
NaAlF <sub>4</sub>	-10.58	-31.23	-10.91	-5.86	-4.29	-446.7
AlHO	1.97	-0.85	6.23	6.33	8.38	-43
AlO <sub>2</sub> <sup>-</sup>	19.45	9.59	17.71	16.03	19.08	-107 ± 30
AlClF <sub>3</sub>	-0.12	-15.06	-0.06	13.42	4.13	-415.87 ± 8
AlCl <sub>2</sub> F <sub>2</sub> <sup>-</sup>	-0.50	-10.89	2.43	1.18	5.50	-367.5 ± 3.1
Al <sub>2</sub> H <sub>7</sub> <sup>-</sup>	22.17	11.40	20.00	30.68	20.10	-14.8
Al <sub>3</sub>	-24.28	-9.10	-20.29	-8.41	-8.54	116.13
C <sub>3</sub> H <sub>9</sub> Al	171.43	242.55	64.97	62.52	64.48	-13.6 ± 2.3
Al <sub>2</sub> S	-16.46	-10.20	-2.75	-1.89	-2.11	34.3 ± 4.9
Al <sub>2</sub> O <sub>2</sub>	-27.36	-21.39	-14.61	-13.66	-10.75	-94.3
C <sub>6</sub> H <sub>15</sub> Al	108.70	110.78	106.92	104.69	107.33	-23.9 ± 1.2
AlF	-2.13	-5.58	0.18	2.44	2.25	-63.5
AlC	-39.29	-34.00	-36.26	-31.99	-34.79	164.8
Al <sub>2</sub> Cl <sub>6</sub>	-4.27	-138.14	-129.14	-127.36	-130.10	-309.7
AlF <sub>3</sub>	-1.67	-15.15	-4.32	-2.15	-1.71	-289
AlCl <sub>3</sub>	-1.87	-1.24	6.48	5.51	5.01	-139.7
MAE <sup>b</sup>	20.31	26.88	17.77	17.12	16.14	
Std <sup>c</sup>	39.62	58.36	35.80	34.93	35.42	
Lar. neg. dev. <sup>d</sup>	-39.29	-138.14	-129.14	-127.36	-130.10	
Lar. pos. dev. <sup>e</sup>	171.43	242.55	106.92	104.69	107.33	

LC-wPBE, PBE1PBE, BMK, M06 and M06-2X are the differences between the experimental data and the LC-wPBE, PBE1PBE, BMK, M06 and M06-2X calculations, respectively

<sup>a</sup>Data from [40] (298.15 K, 1 atm)

<sup>b</sup>MAE is the mean absolute error

<sup>c</sup>SD is the standard deviation

<sup>d</sup>Lar. neg. dev. is largest negative deviation

<sup>e</sup>Lar. pos. dev. is largest positive deviation

<sup>j</sup>Calculations using the aug-cc-pVTZ basis set

(LC-wPBE, PBE1PBE, BMK). This fact was again demonstrated in this paper.

Some of the most extreme values for enthalpies of aluminium compounds are not exclusive for functional. These values represent pathological systems where functionals and basis sets are not sufficient to describe subtle structural and/or electronic effects. Some of these anomalous values were observed from the many papers. Aluminium (or halogenated)

compounds, or molecules containing hypervalent atoms, are usually a source of large deviations. These deviations have constantly been found, and so far have not been solved by functionals and basis sets. Enthalpies of formation for compounds containing these atoms presented a variety of large positive and negative deviations with respect to experimental data. Presently, composite methods are shown to be one of the best options for the calculation of thermochemical

properties, with low computational cost and applicability to chemical systems. These methods incorporate additive corrections to the order of electronic correlations, and some considered extrapolation techniques.

## 4 Conclusion

We have employed the EnAt1 and EnAt2 methods to study the enthalpies of formation for 29 compounds of aluminium. EnAt1 and EnAt2 presented the best results compared to G3X-CEP, G3X(CCSD)-CEP, G4, B3LYP/6-311G(d,p), B3LYP/cc-pVDZ, B3LYP/cc-pVTZ, B3LYP/extrapolation, B2PLYP/cc-pVDZ, B2PLYP/cc-pVTZ, B2PLYP/extrapolation, MP2/cc-pVDZ, MP2/cc-pVTZ, MP2/extrapolation and LC-wPBE, PBE1PBE, BMK, M06 and M06-2X with the aug-cc-pVTZ basis set.

The MAE between the enthalpy of formation (298.15 K) computed at the EnAt1 and EnAt2 levels was quite small, namely 0.14 kcal mol<sup>-1</sup>. In the meantime, the MAE between the enthalpy of formation calculated at the EnAt2 and the M06-2X (best functional calculated) levels was quite large at 13.05 kcal mol<sup>-1</sup>.

In general, average unspecified errors in the enthalpy of formation (298.15 K) have steadily decreased as composite methods with compact effective pseudopotentials (CEP) have evolved. Earlier Gn-CEP composite methods such as G3CEP and G3CEP(MP2) had significantly larger MAE than the EnAt1 and EnAt2 composite methods.

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## References

- Groent CP, Oskam A, Kovács A (2003) Theoretical study of mixed MLaX<sub>4</sub> (M=Na, K, Cs; X=F, Cl, Br, I) rare earth/alkali metal halide complexes. *Inorg Chem* 42:851–858. <https://doi.org/10.1021/ic0260973>
- Laghrissi A, Salmani EM, Dehmani M et al (2016) Ab initio calculations of exchange interactions, Magnetic and optical properties of (Cu, TM)AlO<sub>2</sub> (TM: Ti, V, Cr, Mn and Fe.): LDA and SIC approximation. *Optik (Stuttg)* 127:6991–6996. <https://doi.org/10.1016/j.ijleo.2016.05.024>
- Yang J, Liang F, Cheng Y et al (2019) Improvement of dehydrogenation performance by adding CeO<sub>2</sub> to α-AIH<sub>3</sub>. *Int J Hydrog Energy*. <https://doi.org/10.1016/j.ijhydene.2019.11.086>
- Luo Z, Lei W, Wang X et al (2020) AlF<sub>3</sub> coating as sulfur immobilizers in cathode material for high performance lithium-sulfur batteries. *J Alloys Compd* 812:152132. <https://doi.org/10.1016/j.jallcom.2019.152132>
- Wu H, Chen L, Zhu F et al (2020) The dynamic development of bacterial community following long-term weathering of bauxite residue. *J Environ Sci (China)* 90:321–330. <https://doi.org/10.1016/j.jes.2019.12.001>
- Shunmugasundaram M, Praveen Kumar A, Ponraj Sankar L, Sivasankar S (2020) Experimental investigation and process parameters optimization of stir cast aluminium metal matrix composites to improve material removal rate. *Mater Today Proc*. <https://doi.org/10.1016/j.matpr.2020.01.128>
- Zhang CQ, Liu W (2019) Non-parabolic Al<sub>3</sub>Ti intermetallic layer growth on aluminum-titanium interface at low annealing temperatures. *Mater Lett* 256:126624. <https://doi.org/10.1016/j.matlet.2019.126624>
- Kumar Chauhan P, Khan S (2019) Microstructural examination of aluminium-copper functionally graded material developed by powder metallurgy route. *Mater Today Proc*. <https://doi.org/10.1016/j.matpr.2019.10.007>
- Carey WC, Dixon DG, McDonnell JAM (1985) Space shuttle microabrasion foil experiment (MFE): implications for aluminium oxide sphere contamination of near-earth space. *Adv Sp Res* 5:87–90. [https://doi.org/10.1016/0273-1177\(85\)90390-4](https://doi.org/10.1016/0273-1177(85)90390-4)
- Wu C, Wang B, Wu N et al (2020) Molecular-scale understanding on the structure evolution from melamine diborate supramolecule to boron nitride fibers. *Ceram Int* 46:1083–1090. <https://doi.org/10.1016/j.ceramint.2019.09.075>
- Curtiss LA, Redfern PC, Raghavachari K (2005) Assessment of Gaussian-3 and density-functional theories on the G3/05 test set of experimental energies. *J Chem Phys*. <https://doi.org/10.1063/1.2039080>
- Curtiss LA, Redfern PC, Raghavachari K (2007) Gaussian-4 theory. *J Chem Phys*. <https://doi.org/10.1063/1.2436888>
- Pereira DH, Ramos AF, Morgon NH, Custodio R (2011) Implementation of pseudopotential in the G3 theory for molecules containing first-, second-, and non-transition third-row atoms. *J Chem Phys*. <https://doi.org/10.1063/1.3609241>
- Pereira DH, Ramos AF, Morgon NH, Custodio R (2013) Erratum: “Implementation of pseudopotential in the G3 theory for molecules containing first-, second-, and non-transition third-row atoms” [*J. Chem. Phys.* 135, 034106 (2011)]. *J Chem Phys* 135:219901. <https://doi.org/10.1063/1.3666235>
- Stevens WJ, Basch H, Krauss M (1984) Compact effective potentials and efficient shared-exponent basis sets for the first- and second-row atoms. *J Chem Phys* 81:6026–6033. <https://doi.org/10.1063/1.447604>
- Rocha CMR, Pereira DH, Morgon NH, Custodio R (2013) Assessment of G3(MP2)//B3 theory including a pseudopotential for molecules containing first-, second-, and third-row representative elements. *J Chem Phys* 139:1–13. <https://doi.org/10.1063/1.4826519>
- Pereira DH, Rocha CMR, Morgon NH, Custodio R (2015) G3(MP2)-CEP theory and applications for compounds containing atoms from representative first, second and third row elements of the periodic table. *J Mol Model* 21:204. <https://doi.org/10.1007/s00894-015-2757-3>
- Silva CDS, Pereira DH, Custodio R (2016) G4CEP: a G4 theory modification by including pseudopotential for molecules containing first-, second- and third-row representative elements. *J Chem Phys*. <https://doi.org/10.1063/1.4952427>
- Leal RC, Custodio R (2019) G3(MP2)//B3-SBK: a revision of a composite theory for calculations of thermochemical properties including some non-transition elements beyond the fourth period. *Comput Theor Chem* 1149:1–7. <https://doi.org/10.1016/j.comptc.2018.12.016>
- Silva CS, Custodio R (2018) Empirical corrections in the G3X and G3X(CCSD) theories combined with a compact effective pseudopotential. *Theor Chem Acc*. <https://doi.org/10.1007/s00214-018-2206-3>

21. Silva CS, Custodio R (2015) Investigation of the pseudopotential Stuttgart/Dresden in the G3(MP2, CSSD, rel) theory for compounds containing transition elements. *Rev Process Quimicos* 9:66–67. <https://doi.org/10.19142/rpq.v9i18.258>
22. De Souza Silva C, Custodio R (2019) Assessment of pKa determination for monocarboxylic acids with an accurate theoretical composite method: G4CEP. *J Phys Chem A*. <https://doi.org/10.1021/acs.jpca.9b05380>
23. Nelder JA, Mead R (1965) A simplex method for function minimization. *Comput J* 7:308–313. <https://doi.org/10.1093/comjnl/7.4.308>
24. Becke AD (1988) Density-functional exchange-energy approximation with correct asymptotic behavior. *Phys Rev A* 38:3098–3100. <https://doi.org/10.1103/PhysRevA.38.3098>
25. Lee C, Yang WT, Parr RG (1988) Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys Rev B* 37:785–789. <https://doi.org/10.1103/PhysRevB.37.785>
26. Grimme S (2006) Semiempirical hybrid density functional with perturbative second-order correlation. *J Chem Phys* 124:034108. <https://doi.org/10.1063/1.2148954>
27. Boese AD, Martin JML (2004) Development of density functionals for thermochemical kinetics. *J Chem Phys* 121:3405–3416. <https://doi.org/10.1063/1.1774975>
28. Zhao Y, Truhlar DG (2008) The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, non-covalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other function. *Theor Chem Acc* 120:215–241. <https://doi.org/10.1007/s00214-007-0310-x>
29. Heyd J, Scuseria GE, Ernzerhof M (2003) Hybrid functionals based on a screened Coulomb potential. *J Chem Phys* 118:8207–8215. <https://doi.org/10.1063/1.1564060>
30. Vydrov OA, Scuseria GE (2006) Assessment of a long-range corrected hybrid functional. *J Chem Phys* 125:234109. <https://doi.org/10.1063/1.2409292>
31. Adamo C, Barone V (1999) Toward reliable density functional methods without adjustable parameters: the PBE0 model. *J Chem Phys* 110:6158–6170. <https://doi.org/10.1063/1.478522>
32. McLean AD, Chandler GS (1980) Contracted Gaussian basis sets for molecular calculations. I. Second row atoms,  $Z=11-18$ . *J Chem Phys* 72:5639–5648. <https://doi.org/10.1063/1.438980>
33. Krishnan R, Binkley JS, Seeger R, Pople JA (1980) Self-consistent molecular orbital methods. XX. A basis set for correlated wave functions. *J Chem Phys* 72:650–654. <https://doi.org/10.1063/1.438955>
34. Dunning TH (1989) Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen. *J Chem Phys* 90:1007–1023. <https://doi.org/10.1063/1.456153>
35. Kendall RA, Dunning TH, Harrison RJ (1992) Electron affinities of the first-row atoms revisited. Systematic basis sets and wave functions. *J Chem Phys* 96:6796–6806. <https://doi.org/10.1063/1.462569>
36. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Montgomery JA Jr, Vreven T, Kudin KN, Burant JC, Millam JM, Iyengar SS, Tomasi J, Barone V, Mennucci B, Cossi M, Scalmani G, Rega N, Petersson GA, Nakatsuji H, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Klene M, Li X, Knox JE, Hratchian HP, Cross JB, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Ayala PY, Morokuma K, Voth GA, Salvador P, Dannenberg JJ, Zakrzewski VG, Dapprich S, Daniels AD, Strain MC, Farkas O, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Ortiz JV, Cui Q, Baboul AG, Clifford S, Cioslowski J, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Gonzalez C, Pople JA (2016) Gaussian 09, Revision A.02. Gaussian, Inc., Wallingford
37. Cobos CJ (2002) Heats of formation for AIH, AlOH, OAlH and OAlOH and their monocations. *J Mol Struct THEOCHEM* 581:17–29. [https://doi.org/10.1016/S0166-1280\(01\)00735-7](https://doi.org/10.1016/S0166-1280(01)00735-7)
38. Stewart JJP (2007) Optimization of parameters for semiempirical methods V: modification of NDDO approximations and application to 70 elements. *J Mol Model* 13:1173–1213. <https://doi.org/10.1007/s00894-007-0233-4>
39. Chinini GL, Custodio R (2019) Assessment of a composite method based on selected density functional theory methods and complete basis set extrapolation formulas. *Int J Quantum Chem* 119:1–12. <https://doi.org/10.1002/qua.25892>
40. NIST Chemistry Webbook, <http://webbook.nist.gov/chemistry>

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