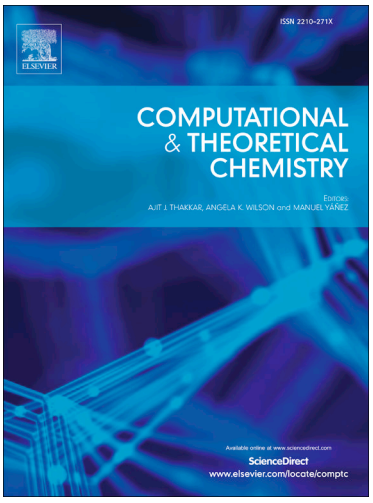

The values of $\Delta_f G^\circ_T(Al_n)$ ($n = 3 – 10$ ATOMS, $T \leq 3000$ K), determined using the ROCBS-QB3 values of $S^\circ_T(Al_n)$ and of the corrected values of $\Delta_f H^\circ_T(Al_n)$

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PII: S2210-271X(18)30286-X
DOI: https://doi.org/10.1016/j.comptc.2018.09.010
Reference: COMPTC 12348

To appear in: *Computational & Theoretical Chemistry*

Received Date: 17 July 2018
Revised Date: 21 September 2018
Accepted Date: 22 September 2018

Please cite this article as: G.A. Poskrebyshev, The values of $\Delta_f G^\circ_T(Al_n)$ ($n = 3 – 10$ ATOMS, $T \leq 3000$ K), determined using the ROCBS-QB3 values of $S^\circ_T(Al_n)$ and of the corrected values of $\Delta_f H^\circ_T(Al_n)$, *Computational & Theoretical Chemistry* (2018), doi: https://doi.org/10.1016/j.comptc.2018.09.010

THE VALUES OF $\Delta_f G^o_T(Al_n)$ (n = 3 – 10 ATOMS, $T \leqslant 3000$ K), DETERMINED USING THE ROCBS-QB3 VALUES OF $S^o_T(Al_n)$ AND OF THE CORRECTED VALUES OF $\Delta_f H^o_T(Al_n)$

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Abstract. In the present work, the values of $\Delta_f G^o_T(^kAl_n)_{CORR}$ have been determined on the basis of the thermochemistry of atomization reactions ($\Delta_r G^o_T(^kAl_n \rightarrow n^2Al) = \Delta_r H^o_T(^kAl_n \rightarrow n^2Al) - T\Delta_r S^o_T(^kAl_n \rightarrow n^2Al)$), calculated using the ROCBS-QB3 values of $S^o_T(^kAl_n)$ and corrected values of $\Delta_f H^o_T(^kAl_n)_{CORR}$ as well as of the tabulated values of ^2Al. The values of $\Delta_f H^o_T(^kAl_n)_{CORR}$ have been determined using the temperature dependencies of ROCBS-QB3 values of $\Delta_f H^o_T(^kAl_n)$, calculated at $T \leq 3000$ K, and the corrected values of $\Delta_f H^o_{298.15}(^kAl_n, 2 < n \leq 10 \text{ atoms})_{CORR}$, determined using the perfect linear correlation dependence, proposed in the present work for the clusters X_m ($m \leq 8$ atoms), formed by the elements of the third row of the periodic table of elements (X = Na, Mg, Si, S, P and Cl, $m \geq 2$ atoms).

The values of $\Delta_f H^o_{298.15}(^kAl_n, 2 < n \leq 10 \text{ atoms})_{CORR}$ and $\Delta_f H^o_0(^kAl_n, 2 < n \leq 10 \text{ atoms})_{CORR}$ have been in good agreement, respectively, with the values of $\Delta_f H^o_{298.15}(^kAl_n, 2 < n \leq 10$ atoms), determined using the ROCBS-QB3 and CBS-Q thermochemistry of isodesmic and non isodesmic reactions, as well as with the theoretical values of the cohesive energies, reported previously. The CBS-Q and CBS-QB3 approaches have not been used for the calculations of the values of $\Delta_f H^o_T(^kAl_n, 2 < n \leq 10$ atoms) due to the spin contamination problems.

At the same time, the effect of the spin contamination on the values of $S^o_{298.15}(X_m)$ has not been significant, and has not been expected for the values of $S^o_{298.15}(^kAl_n)$. The values of $S^o_{298.15}(X_m)$ and $S^o_{298.15}(^kAl_n)$, calculated using the different QM approaches (CBS-Q, RO/CBS-QB3, LSDA, PBEPBE, MP2) have been in the agreement each with the others. However, the more consistent values of $S^o_{298.15}(^kAl_n)$ have been determined using the correlation dependencies between the tabulated and calculated values of $S^o_{298.15}(X_m)$.

The values of $\Delta_f G^o_T(^kAl_n, n > 4$ atoms), calculated in the present work, have been up to 250 kJ/mol higher those theoretical values, reported previously. The corresponding values of equilibrium constants $(K^o_p)_{n-1}$ of reactions $^kAl_n = {}^2Al + {}^{k\pm1}Al_{n-1}$ ($n > 3$ atoms) indicate that the contribution of the ^kAl_n clusters to the gas phase oxidation of ^2Al is insignificant.

Keywords: Al_n, Heat of formation, Free energy, entropy, ROCBS-QB3, Correlation dependence.