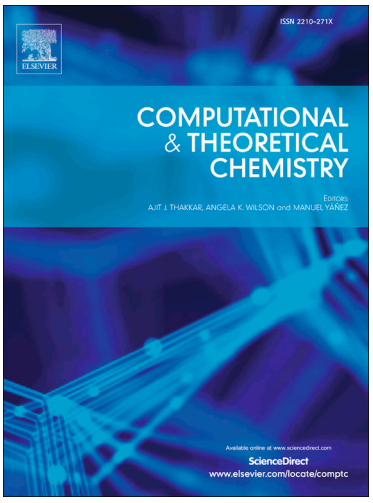
Accepted Manuscript



RE-EVALUATION OF THE STANDARD THERMOCHEMICAL PROPERTIES OF THE Al_2 CLUSTER ON THE BASIS OF CBS THERMOCHEMISTRY OF ISOGYRIC REACTIONS AND CORRELATION DEPENDENCIES

Gregory A. Poskrebyshev

PII: S2210-271X(18)30077-X
DOI: https://doi.org/10.1016/j.comptc.2018.03.001
Reference: COMPTC 2735

To appear in: *Computational & Theoretical Chemistry*

Received Date: 16 February 2018
Revised Date: 1 March 2018
Accepted Date: 3 March 2018

Please cite this article as: G.A. Poskrebyshev, RE-EVALUATION OF THE STANDARD THERMOCHEMICAL PROPERTIES OF THE Al_2 CLUSTER ON THE BASIS OF CBS THERMOCHEMISTRY OF ISOGYRIC REACTIONS AND CORRELATION DEPENDENCIES, *Computational & Theoretical Chemistry* (2018), doi: https://doi.org/10.1016/j.comptc.2018.03.001

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RE-EVALUATION OF THE STANDARD THERMOCHEMICAL PROPERTIES OF THE Al_2 CLUSTER ON THE BASIS OF CBS THERMOCHEMISTRY OF ISOGYRIC REACTIONS AND CORRELATION DEPENDENCIES

Gregory A. Poskrebyshev
Institute of Energy Problems of Chemical Physics, Russian Academy of Sciences, Russian Federatian, Moscow, Leninsky prosp., bldg. 38-2

Abstract. In the present study, the value of $\Delta_f H^o_{298.15}(^3Al_2(^3\Pi_u))_{atom}$ = 518.4, 521, 521.4, 521.3 and 517.7 kJ/mol have been calculated using, respectively, CBS-QB3, ROCBS-QB3, W1U, W1RO and CBS-Q approaches. The slightly lower values of $\Delta_f H^o_{298.15}(^3Al_2)_{isog}$ = 495±15, 513±7, 503±17, 513±9 and 507±8 kJ/mol have been determined, respectively, by the same quantum mechanical approaches, but on the basis of thermochemistry of the isogyric reactions. The higher values of $\Delta_f H^o_{298.15}(^3Al_2)_{CORR}$ = 522.8 (CBS-QB3), 521 (ROCBS-QB3), 520.4 (W1U), 521.3 (W1RO) and 519.7 (CBS-Q) kJ/mol have been determined on the basis of the correlation dependence between tabulated and calculated values of the bond dissociation energy (*BDE*) of compounds contained double and triple bonds. The close value of $\Delta_f H^o_{298.15}(^3Al_2)$ = 525 kJ/mol have also been determined within ROCBS-QB3 approach, on the basis of the perfectly linear correlation dependence between tabulated and calculated values of the *BDE* of dimers, formed by elements of the third row of the periodic table of elements. In contrast, the significantly higher value of $\Delta_f H^o_{298.15}(^3Al_2)_{CORR}$ = 549.9 kJ/mol have been determined on the basis of the correlation dependence between tabulated and theoretical values of BDE calculated for the lowest triplet states of B_2, Al_2 and Ga_2. Such high difference, observed in the last case, has been attributed to the high uncertainty in the tabulated/experimental values of $\Delta_f H^o_{298.15}(^3B_2)$ and $\Delta_f H^o_{298.15}(^3Ga_2)$. As a result, the lowest limit of the experimental values of $\Delta_f H^o_{298.15}(^3Al_2)$ = 525 kJ/mol and $\Delta_f H^o_{298.15}(^3Ga_2)$ = 430 kJ/mol, as well as the upper limit of the value of $\Delta_f H^o_{298.15}(^3B_2)$ = 851.2 kJ/mol have been accepted as the best available estimate.

The temperature dependence of $\Delta_f H^o_{298.15}(^3Al_2)$, has been calculated using the ROCBS-QB3 approach.

The value of energy gap *E*(S-T) = 31.8, 29.6 and 29.1 kJ/mol between the lowest triplet ($^3\Pi_u$) and singlet ($^1\Sigma_g^+$) states of Al_2 have been determined using, respectively, CBS-Q, ROCBS-QB3 and W1RO calculations. The slightly different values of *E*(S-T) = 32.1±6, 28.9±7 and 25.6±4 kJ/mol have also been determined using correlation dependencies. The last of these values has been considered as the most accurate.

The values of $S^o_{298.15}(^3Al_2)$ = 236.6±0.1 J/(mol K) and its temperature dependence, calculated in the present work, agree with those reported previously.

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