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COMMENT/REPLY

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Reply to Comments by O. V. Dorofeeva on *J. Chem. Eng. Data* 2010, *55*, 5359−5364

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S *Supporting Information*

We thank Dorofeeva for her comment[1] which may stimulate some fruitful discussion among the scientific community. There are at least two different atomization methods being employed in the literature to arrive at 298.15 K gas phase enthalpies of formation, and they do yield slightly different results. A brief review of the literature obtains a sample list of atomization energy publications given in the Supporting Information, in which the following range of approaches are used: (1) the form of the atomization method[2−4] recommended by Dorofeeva or its equivalent; (2) analogous calculations to those presented by Saeys et al.;[5] (3) variations of (1) or (2) using various corrections or modifications to the energies chosen; and (4) methods insufficiently described to be clearly determined (or reproduced) with the information provided (including in the respective Supporting Information), potentially being hybrids of (1) and (2) and/or sometimes using nonstandard fundamental properties (e.g., atomic enthalpies of formation). We have chosen not to classify this representative list of publications based on the inferred method employed so we may avoid implying any bias or errors in any of these works. Readers should be able to readily classify most works based either on atomization method referencing by the authors concerned (generally limited to studies using the approach in refs 2 to 4) or deduced by the energies/enthalpies provided by the authors (e.g., the experimental and theoretical atomic enthalpies of formation given, their associated temperatures, the presence/absence of any (0 to 298.15) K correction factors, and 0 K and/or 298.15 K theoretical molecular data). As shown in the comment,[1] for compounds ranging in size between cyclopropane and toluene, the deviation between the two primary approaches is between (0.2 and 0.6) kcal·mol^{-1} ((1.0 to 2.6) kJ·mol^{-1}). In our original work,[6] we used the atomization method described by Saeys et al.[5] There is adequate information given in Saeys et al.[5] (including equations, thermodynamic cycle schematics, and atomic enthalpies employed by these authors; e.g., see pages 9149−9151 in this reference) to allow readers to reproduce their calculations and use the approach for other compounds and levels of theory.

As part of this reply to the comment, we conducted CBS-Q//B3[7,8] level calculations using Gaussian 09[9] (G09) on methane, ethyne, ethene, ethane, propyne, propene, and benzene (G09 archive entries provided in the Supporting Information), as well as on the corresponding carbon and hydrogen atoms, to confirm that the atomization energy approach derived enthalpies of formation ($\Delta_f H^\circ_{(g)}$) given in ref 5 could be reproduced using their conceptual methods and same level of theory (although these authors used Gaussian 98). We found the following deviations ranging from (0.1 to 0.4) kJ·mol^{-1} ((0.0 to 0.1) kcal·mol^{-1}) between the reported CBS-Q//B3 $\Delta_f H^\circ_{(g)}$ from ref 5 using the atomization method given therein and our G09-CBS-Q//B3 calculations (all $\Delta_f H^\circ_{(g)}$ values given in kJ·mol^{-1}; cw = current work): methane, −74.1,[5] −74.2;[cw] ethyne, 234.5,[5] 234.4;[cw] ethene, 56.0,[5] 55.9;[cw] ethane, −81.9,[5] −82.0;[cw] propyne, 192.0,[5] 191.9;[cw] propene, 25.7,[5] 25.5;[cw] and benzene, 91.0,[5] 90.6.[cw] If the atomization approach referenced[2−4] in the comment[1] is used for these compounds at the CBS-Q//B3 level of theory, the following $\Delta_f H^\circ_{(g)}$ are obtained (all values are in kJ·mol^{-1}; deviations from the atomization approach given in ref 5 using our data are given in brackets): methane, −74.5 [−0.4]; ethyne, 233.7 [−0.7]; ethene, 55.2 [−0.7]; ethane, −82.7 [−0.7]; propyne, 190.9 [−1.0]; propene, 24.5 [−1.0]; and benzene, 88.5 [−2.0].

Consequently, there is a small systematic difference with general molecular weight scaling effects between $\Delta_f H^\circ_{(g)}$ obtained using the atomization method outlined by Saeys et al.[5] when compared to the atomization approach provided in refs 2 to 4. For organic compounds currently in the practical range of Gaussian-4 (G4) calculations, the estimated $\Delta_f H^\circ_{(g)}$ differences between the two atomization energy methods appear to be less than assumed errors (i.e., chemical accuracy of ± 4.2 kJ·mol^{-1} [1 kcal·mol^{-1}]) inherent in the calculations and corresponding experimental data. In the Supporting Information, we provide G4 and W1BD estimated $\Delta_f H^\circ_{(g)}$ using both atomization methods for comparison (as well as 0 K energies and 298.15 K enthalpies for all compounds in ref 6). Differences in $\Delta_f H^\circ_{(g)}$ between the two approaches at the G4 level range from (0.4 to 3.8) kJ·mol^{-1}. Using the atomization method in refs 2 to 4, we obtain effectively equivalent $\Delta_f H^\circ_{(g)}$ to the G4 level work of Curtiss et al.[10] for the subset of compounds referred to in Table 1 of the comment.[1]

We acknowledge that the conformation of cyclopropylbenzene in ref 6 was not the global minimum, and we thank Dorofeeva for bringing this to our attention. The MMFF94[11] conformational analysis used in ref 6 results in a predicted molecular mechanics global minimum that leads (during the G4 geometry optimization process) to a G4 optimized conformation

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that is 3.8 kJ·mol^{-1} (0.9 kcal·mol^{-1}) above the global minimum. A revised G4 geometry for cyclopropylbenzene is given in the Supporting Information, and the updated $\Delta_f H°_{(g)}$ (using both atomization methods) is provided in Table S3 (along with the revised 0 K energy and 298.15 K enthalpy in Table S1). We have also included visualizations of all G4 optimized geometries from ref 6 in the Supporting Information. A review of the geometries under study suggests that cyclopropylbenzene is one of the most (if not the most) conformationally challenging structures in our database. If readers feel that an optimized structure is not the global minima for a particular compound, ref 6 provides all final geometries to aid in a rigorous re-evaluation of our findings.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. A sample list of atomization energy publications, CBS-Q//B3 level calculations using Gaussian 09, G4 and W1BD estimated $\Delta_f H°_{(g)}$ using both atomization methods, and visualizations of all G4 optimized geometries from ref 6. This material is available free of charge via the Internet at http://pubs.acs.org.

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