Response to Reviewers

Reviewer B

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| # | Reviewer’s comments | Authors’ response |
| 1. | The title of the manuscript is misleading - it indicates employment of semi-empirical quantum chemical methods. It should be adjusted to the content of the manuscript. | Thank you for the comment, we agree with you. The new title is **Empirical method for predicting the enthalpies of combustion of amides.** |
| 2. | It should be clearly stated that Equation 1 results from experiments presented in the current manuscript. | We agree. Therefore, in lines 61-62 we inserted the words:  “The experimental values of the enthalpies of combustion of the amides studied by us are presented in Table I in the ‘results and discussion’ section.” |
| 3. | It would be helpful to write a general formula for a combustion reaction in order to show what "n" in Equation 1 stands for. | Yes. Thank you for the suggestion. We included this in lines 66-71:  “Inside the calorimeter, the process of complete combustion of amides takes place according to the general equation:  CaHbOcNd +(n/2)O2 = aCO2 + (b/2)H2O+(d/2) N2  (1)  We compared the enthalpies of combustion of the studied amides and the number of oxygen atoms n = 2a + b/2-c required for the complete combustion of one mole of the studied amide (Table 1) and found a simple regularity that relates these quantities to each other” |
| 4. | I do not agree with the Equation presented in line 93, since it implies that the enthalpy of combustion would increase by the same amount regardless whether the molecular formula changes by, for example, four carbon atoms, four nitrogen atoms, or four hydrogen atoms. On the other hand, agreement between estimated and measured results is satisfactory, which justifies employment of Equation 1. Since the method is semi-empirical, I suggest that the authors omit the discussion presented in lines 88-93. | As suggested, we omitted the discussion presented in lines 88-93. Also, in order to move from purely mathematical reasoning to chemical reasoning we wrote in lines 74-76 that “The observed dependence makes it possible to clarify the physicochemical meaning of the found correlation (2) and examine the accuracy of predictive calculations based on it (Table I).” |
| 5. | Why does the relative deviation depend only on the mole fraction of nitrogen atoms and not on the mole fractions of carbon, hydrogen or oxygen atoms? I suggest that the authors explore the possibility that the relative deviation also depends on the mole fraction of other atoms. | In order to emphasize the different roles of carbon and hydrogen atoms on the one hand, and nitrogen atoms on the other, we wrote in lines 83-99: “The more CH groups are in the amides, the more carbon dioxide and water will be formed as a result of combustion, and the greater number of oxygen atoms n is necessary for their formation. If the process of complete combustion of amides was accompanied by the formation of nitrogen oxides, it would be similarly assumed that the more nitro groups are in the amide formula, the more oxygen is needed for the combustion of amides. As can be seen from the general equation for the combustion of amides (1), this is not the case. Therefore, according to Table I, it is easy to find out that with an increase in the number of nitro groups in the amide formula, the relative deviation of the predicted values from the experimental values of the enthalpy of combustion increases. However, on the other hand, it can be seen from the same table (Table I) that the relative deviations of the calculated values of the enthalpies of combustion of amides from the experimental values do not exceed 2.5%, which indicates a sufficient reliability of the prediction method.  The logic of the reasoning and the good agreement between the predicted and experimental values of combustion enthalpies (Table I) allow to assume that the molar fraction of nitrogen atoms in the amide formula might serve as a certain quantitative limiting factor that would indicate the upper margins of the relative deviation of the predicted and experimental values of the enthalpy of combustion.” |
| 6. | Since the correlation coefficient exceeds 0.9, why is there such large discrepancy between the experimental and theoretical relative deviation? It amounts to an order of magnitude. | The relative deviations of the values of the enthalpies of combustion calculated by the correlation (2) (in the revised version it is numbered as 2, in the first version it is numbered as correlation 1) are much smaller than the estimate of the upper margin of such deviations. This is consistent with the logic, which states that “the molar fraction of nitrogen atoms in the amide formula might serve as a certain quantitative limiting factor that would indicate the upper margins of the relative deviation of the predicted and experimental values of the enthalpy of combustion.” Although the relative deviations of the predicted values from the experimental ones are an order of magnitude lower than the quantitative estimate of the upper margin of such deviations, calculated using correlation (3) (this correlation is numbered as correlation 2 in the first version of the manuscript).  We emphasized this again in lines 100-106: “In this regard, we calculated the correlation coefficient between the relative deviation and XN - the molar fraction of nitrogen atoms in the amide, it turned out to be rather high and equal to 0.929; thus, based on the regression analysis, the following relationship was obtained:  = 12.ХN  (3)  on the basis of which, it is possible to estimate the expected maximum errors of the predicted values of the enthalpies of combustion of amides calculated by the formula (2).” |
| 7. | The significance of the proposed formula should be more thoroughly discussed in the Conclusions. For example, the authors might emphasize good agreement with experimental data despite its very simple form. | Yes, thank you. We wrote in lines 113-116: “As can be seen from Table II, the values given in the literature and the calculated values are in a good agreement with each other. The table also shows that the relative deviations of the predicted values from the experimental values do not exceed the upper margin of the relative deviations calculated by the formula (3).” Also, we rewrote the conclusion and states there that “The good agreement between the predicted values of the enthalpies of combustion of amides calculated by correlation (2) and the experimental values suggests that researchers can use the methods proposed above to predict the enthalpies of combustion of amides for which there is no reliable experimental data, and to predict the expected marginal error in calculating these quantities. Technologists can also use these methods for carrying out engineering calculations.” |
| 8. | It is not clear whether reference 4 corresponds to a dissertation or an article. Furthermore, the presented references are rather old, apart from reference 5. | This was an article, but there was an error in the title of the journal, but it doesn’t matter anymore. Because we agree that the links are old, we removed all the old links that relate to this manuscript only indirectly and left those that are directly related to this publication and replaced one of them with a newer 2005 source. | |

Reviewer C

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| # | Reviewer’s comments | Authors’ response |
| 1. | There are eight references listed, but only one is from 2018. The other seven are from 19.. Please, add some fresh references. | We agree; therefore, we removed all the old references that relate to this manuscript only indirectly and left those that are directly related to this manuscript and have replaced one of them with a newer source of 2005. |
| 2. | In the EXPERIMENTAL part, (line number 58) there is a sentence: Moreover, the amount of material was chosen so that the temperature rise in the experiment corresponded to the temperature rise when the reference substance was burned [2]. Please, clarify this | Instead of lines 58-59, we wrote: “Moreover, the amount of substance was chosen as recommended in the reference literature” and inserted a reference to a reference book edited by Kolesov (ref #3 in the revised version). We did not describe in detail the methods for selecting the mass of a sample, and limited ourselves to the fact that this is a common technique, since we believe that the topic of the manuscript is prediction and the method for calculating the enthalpies of compounds of still unexplored by the calorimetric method compounds. |
| 3. | In Table I, one of the listed columns is n, number of oxygen atoms needed for complete combustion. Please explain, in detail, how this was calculated? | Thank you for the comment. We took this into consideration and in lines 66-71 we wrote: “Inside the calorimeter, the process of complete combustion of amides takes place according to the general equation:  CaHbOcNd +(n/2)O2 = aCO2 + (b/2)H2O+(d/2) N2  (1)  We compared the enthalpies of combustion of the studied amides and the number of oxygen atoms n = 2a + b/2-c required for the complete combustion of one mole of the studied amide (Table 1) and found a simple regularity that relates these quantities to each other” |
| 4. | Part of the text from line number 86 to line number 99 > I suggest that this part of the manuscript should be rewritten with special attention given to clarify formulas and text. Please number the equations. It is unclear how consecutive formulas are derived one from another. What does small h means? | A small h was a typo, a large H should have been in its place, but this no longer matters, since we completely replaced the mathematical formulas with more understandable and simple chemical explanations. |