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Biogeosciences Discussions

Interactive comment on "Group additivity calculation of the standard molal thermodynamic properties of aqueous amino acids, polypeptides and unfolded proteins as a function of temperature, pressure and ionization state" *by* J. M. Dick et al.

Anonymous Referee #3

Received and published: 18 December 2005

Review of "Group additivity calculation of the standard molal thermodynamic properties of aqueous amino acids, polypeptides and unfolded proteins as a function of temperature, pressure and ionization state" by Dick, J. M., LaRowe D. E. and Helgeson H. C.

Summary

The authors describe a method to calculate the properties of aqueous biomolecules at wide ranges of temperature and pressure. These data are necessary for determining

reaction properties among biomolecules in aqueous environments.

General Comments

The paper is very well-written, and data of this type is highly desirable in the biogeochemical community. As such, this research constitutes a significant contribution to the biogeochemistry literature and will be a well-referenced paper and is sure to find its place among many similar papers. On the other hand, the paper is probably overly long, and this reviewer has difficulty with some of the ways in which this information is presented. Additionally, there are instances where better explanation of some of the calculations would be helpful. Finally, it is unclear how useful these calculation methods will be in 'real' biochemical calculations due to limitations on the types of reactions that can be investigated. Proteins do not really exist in nature in an unfolded state, and therefore the usefulness on properties of the unfolded state is limited.

Overall, this is a great contribution. These data are long overdue. The paper is logical, the methods are solid, and a great deal of attention has been paid to make sure that this paper can be used by a wide audience, including biochemists and geochemists.

I recommend that this paper be published with relatively minor revision. The paper would benefit from example calculations, illustrations of the structures being discussed, and easier to read figures and tables. The appendices seem to be excessively long or redundant from earlier literature. In particular, Appendix A contains the revised HKF equations of state, which have been published numerous times in the geochemical literature and really does not need repeating here. I

Specific Comments

Pages 1518-1522, Section 2: Examples of the structures of the compounds being described here would be very helpful. This section is very descriptive, but is very dry and it is sometimes difficult to envision exactly how these molecules are put together. This is especially true for geochemists who have limited knowledge of the chemistry of

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biomolecules.

Page 1519, line 10: The word "thermodynamic" is misspelled.

Page 1520, line 9: "Ěto generically identifyĚ" is a split infinitive.

Page 1523, line 25: Insert the word "in" before the symbol "V°."

Page 1524, line 21: I think there should be a "D" symbol before "V°n".

Page 1524, line 25: There is a missing degree symbol after the DVn.

Page 1525, line 10: There is no reference for Hedwig et al. (which should have a date here in the text) in the reference list.

Page 1525, line 22: The word "expansibility" is misspelled.

Page 1525, line 26: There should be a reference for SUPCRT92 (Johnson et al., 1992).

Page 1526, line 16-17: Is the delta symbol before the Cp° correct? If so, should there be one before the V° in line 17?

Page 1528, line 3: Remove either the word "by" or the word "from."

Page 1532, line 2: "aforementioned" should be one word.

Page 1534, line 19: Remove the comma after the words "Table 10".

Page 1536, line 7: The word "destruction" is misspelled.

Page 1544, line 24: Change the word "is" to "are" (data is plural!).

Page 1544, line 26: Remove the final letter "s" from the word "seems".

Page 1545, line 17: Add the letters "ly" to the end of the word "substantial".

Page 1545, lines 20-22: The text in parentheses is not a sentence.

Page, 1546-1547, Conclusions: The authors should comment a bit more on the useful-

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ness, but more importantly, the limitations of these data. Until they can account for the disulfide bond contribution to proteins, and the folded state, these calculations are of limited value for proteins. If the authors have an example where knowing the properties of unfolded proteins is of significance, they should provide it.

Page 1548, Appendix A: As mentioned in the general comments, this appendix is redundant to the literature, and should probably be removed. Can't this just be referenced?

Page 1554, line 10: There is a missing left parenthesis.

Page 1555, line 18: The word "contributions" is misspelled.

Page 1555, line 20: Insert a period after the word "diamines".

Page 1556, first paragraph: The authors should indicate that Equations B1-B9 are found in Table 13. It took me a while to figure that out!

Page 1557, line 18: The ˜ symbol should not appear in superscript.

Page 1557, line 29: Change the word "which" to the word "that".

Page 1559, line 5: Remove the word "the" before the word "generally".

Page 1559, line 6: Is 100 K correct, or should the unit be °C?

Page 1560, line 19-21: What is the value of the temperature of transition for leucine? The temperatures of these data are awfully low, and I disagree that the two term Maier Kelley is sufficient.

Page 1560, line 16: The word "maintain" is misspelled.

Page 1562, line 12: Remove the word "a" from before the word "solutions".

Page 1562, line 13: I am not sure that "In the future" is the way to begin this sentence.

Page 1562, line 18: Insert the word "of" between the words "lessening" and "the".

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Interactive Comment

After Appendix D, some example calculations of the properties in question might be useful to include. This could also be added to the text immediately before the Conclusions section.

Page 1569, line 27: The word "Gibbs" should be capitalized here unless it was done incorrectly in the reference.

Page 1570, line 27: The word "hyperthermophilic" is misspelled.

Page 1572, lines 1-2: Check the title of this article to see if it is correct.

Page 1578, line 3: The word "Unless" is misspelled.

Page 1585, line 1: This table caption contains too many "ands", making it difficult to decipher.

Page 1589, Table 11: The superscripted footnote symbols in this table are extremely difficult to read. Perhaps an additional column with the references is in order.

Page 1594, Footnotes: These should start flush with the bar immediately above, or be centered under the table itself (and not the caption).

Figures: Many of the figures are too small to see clearly. This is an especially acute problem when multiple plots are presented as one figure. For example, Figure 2 contains 12 plots, each of which is difficult to read. While it is perfectly acceptable to present the information this way, perhaps the figure itself should be much larger. There are many other examples in which this is the case.

Additionally, in many of the figures, the symbol for the amino acid being plotted are given next to the axisĚin a number of instances, these symbols overlap or are on top of the plot frame, making them very difficult to discern (see especially Figures 2, 3, 4, 7, 8, and 10).

Figure 2 caption, line 6: The name "Hedwig" is misspelled.

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Figure 3, top left plot: I am unconvinced by the regression line for amino acid A. The data at high temperature are not consistent with the line.

Figure 3 caption, line 6: The name "Hedwig" is again misspelled.

Figure 6: The letters inside these symbols are very difficult to see.

Figure 11: I am somewhat confused by what the lines here represent, the entire set of data regressed? If so, then for all but the plot at lower right these fits are a bit difficult to accept. This is also true for the plots in Figure 12, especially those plots upper and lower left. These are not really very good representations of these data.

Figure 16 caption: The (top) and (bottom) designations should actually be (left) and (right) throughout this caption.

Figure 16: The fits of the curves on both of these plots is really not very good. I realize that these are the best methods of calculating these properties, but I am not very impressed.

Figure 17 caption, lines 4 and 5: The same symbol is listed for values from two different references. One of them should be a filled circle?

Figure 17, middle left plot: The curve doesn't go anywhere near the experimental symbols. Is this a problem with the parameters, or is there something more fundamental going on?

Figure 18: The data indicate that there is a major upturn starting at about 320K here. What is the transition temperature of leucine? This does not bode well for the assumption that the heat capacity function of the amino acids is acceptable with c=0 on the Maier Kelley equation. Why not include it?

Figure 19: These plots are just too small.

Figure 19: A couple of the correlations in these plots are not convincing at all, especially in noting the error bars on the symbols.

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Interactive Comment

Interactive comment on Biogeosciences Discussions, 2, 1515, 2005.