

Interactive comment on “A two-dimensional volatility basis set: 1. organic-aerosol mixing thermodynamics” by N. M. Donahue et al.

N. M. Donahue et al.

nmd@andrew.cmu.edu

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I did not manage to get all the way through this ms. The work that is presented here is either simple, but rendered complex and hard to grasp by the authors' obscure description, or it is actually complex and made more so. It would be hard for anyone, except the authors, to make full use of the results valuable though they may be.

Not surprisingly that was not our intent. While Reviewer 1 does not appear to have shared the confusion of this reviewer with our presentation, our intention is to convey as simple a message as possible to as wide an audience as possible. It is thus extremely useful to encounter readers who have difficulty with a manuscript. The introductory material in our original submission was meant as that – a simple introduction to lay the groundwork for what we really wanted to present. That strategy clearly failed, as our

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attempt entangled this reader.

Because of the difficulty this reviewer had with our original presentation, we have reorganized the manuscript. Our main objective is to present (and defend) the basis for the curves of constant carbon and oxygen number now presented in Fig. 4 (originally Fig. 5 and 8). We want it to be clear that the question we are asking is the inverse of the one usually asked. Rather than asking “given a compound of such and such structure in a mixture of so and so composition, what is the partial pressure?” we ask “given material of some volatility and oxygen content (O:C), what is the composition (carbon and oxygen number)?”

The way the paper is now structured, a reader could read through the end of Section 2 and stop. The result would be a good understanding of the empirical basis for our 2D-VBS at the level of ideal mixing. However, we do feel that to pose the question of how to deal with activity coefficients while confronting the complexity and indeed the mean characteristics of ambient aerosols is a valid and important topic. Here, we are asking, “within the constraints of this 2D-VBS formulation, can we reasonably describe activity coefficients?” The answer may be “no”, as the reviewer asserts, but the review does not go beyond that simple assertion of doubt.

The abstract. This ought to offer a self-contained description of the results, that can be understood without reference to other papers or to other parts of the ms.

We have re-written and shortened the abstract.

(1) C^o is known well enough by those familiar with the authors' work, but for those who are not it is insufficiently defined by only the words "saturation concentration".

We added “mass” to make the line read “saturation mass concentration”.

(2) The expression “mean field approximation” adds nothing here, and I'm not clear what the authors intend. (3) “we show that a linear structure activity relation (SAR)... is directly tied to ideal solution .. behaviour.” I am almost certain that this sentence is

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meaningless. (4) “..slightly non-linear SAR emerge from off-diagonal (carbon-oxygen) interaction elements.” Again, impossible to get any significant meaning from this. “Off-diagonal” is a piece of jargon related to the authors’ use of a matrix for interactions later in the ms.

These passages are no longer included in the abstract. They are meaningful, but as the reviewer points out the abstract is not the place to engage that debate.

(5) *I doubt very much that an approximate treatment such as that being proposed here would be able to predict phase separation with any accuracy.*

We can’t do very much with this. We believe that our formulation of the activity coefficient is valid and self-consistent, and that this formulation can be tested. It seems worth subjecting the reviewer’s doubt to experimentation.

(6) *OA not defined.*

It is defined the first time it is used.

Introduction (1) microgm-3 is not a unit, but microg m-3 is (space before "m"). This error is common.

This is and was written

$\mu g \ , \ m^{-3}$

throughout. That is the correct T_EX, with the “\,” producing a space. The rendered manuscript does have space between the “μg” and the “m”, though as typical of L^AT_EX the exact space varies. The comment is gratuitous.

(2) *An annoyance: don’t invent your own terminology where one already exists. Writing $\log_{10}(C^*)$ as lC^* is unnecessary and potentially confusing for reasons that are obvious.*

It is very common to present a variable substitution, especially when one is linearizing a
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problem. The literature is appropriately full of symbols defined by authors. However, we certainly do not want to confuse, and we have replaced all occurrences with $\log_{10} C^o$.

(3) *The complexity of the organic portion of the aerosol, and our partial knowledge of its composition, is a difficulty that has helped determine the approach the authors (and others) have taken. However, it is not “the challenge we seek to confront.”*

(4) *“SAR” is not an accurate expression as the authors’ approach does not seem to involve any explicit structural information.*

We have replaced all references to “structure activity” with “group contribution”.

(5) *nC, nH etc not defined. These would normally mean numbers of moles, but appear to mean numbers of atoms.*

These terms are now defined when they are introduced.

(6) *A contradiction: “a generalised prediction of activity coefficients for individual organics will fall out naturally and self-consistently from this formulation” is followed a few sentences later by: “We do not seek to accurately predict the phase partitioning of specific molecules. ...we seek to understand the bulk behaviour of OA.”* (7) *More idiosyncratic jargon: “rich behaviour”.* (8) *“..carbon-oxygen cross interaction (the hydrophobicity)”. The word hydrophobic refers specifically to water whereas the interaction is general.*

We reworked the closing paragraphs of the introduction.

Theory I have two general objections: first, the authors are attempting to develop an activity coefficient scheme within a system of mass-based concentrations. I won’t say this is impossible, but it is a fundamental difficulty that is not explained. Consequently, I have to wonder whether the authors’ exposition that includes “pseudo-Arrhenius”, “Boltzmann term” and a division by the gas constant to “scale” energies that are used in expressions with quantities that have units of $\mu g m^{-3}$, is correct - or whether the use of these terms just lends the text an air of spurious thermodynamic respectability.

We have moved the simple theory section to an appendix because it is not needed until we attempt to say something about activity coefficients near the end of the paper. We do feel, however, that the terms we use are defined precisely and used accurately. Our perspective on this problem is that we simply cannot determine the molar abundance of various constituents in organic aerosol because we don't know the number of moles of organics in the OA. All desire of pure theory notwithstanding, this is the basic issue we have to confront if real atmospheric measurements are a constraint. We believe that we don't oversell what we are trying to do here – instead, we are trying to see how far we can get with the information we do have. We *do* argue that it appears this presentation may be quite useful.

Second, there are very many activity models in existence, and of varying degrees of complexity and suitability for application to organic aerosols in general and to the problem the authors are trying to solve in particular. Beyond passing reference to UNIFAC there is no mention of any of them. I suspect that it would have been possible to adapt some of these to the present problem and to do so in a way much more easy to understand – and much more clearly related to existing theory and thermodynamic principles – than what the authors have developed.

All of the treatments we have encountered are built around surrogate molecules – we would be happy if the reviewer provided any guidance. Even the simple idea of a mole fraction is impossible to define for ambient organic aerosol. We have no idea how many moles are present in organic-aerosol particles because we don't know the composition of the organic compounds comprising the aerosol. That is really the whole point of this paper, which we failed to convey to this reviewer. For that reason, we have re-organized the manuscript to get to Fig. 4 quickly before any discussion of activity coefficients is presented.

In the remaining parts of the theory section, before I completely lost track of what the author's were trying to do, I noted: (1) In eq (7) the introduction of a matrix – do they just mean a summation of the different interactions?" (2) $i \rightarrow A$. I don't think "i" tends to

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"A" at all. (3) "We shall assume that ... with the fractions of A and B in the solvent." This assumption comes completely out of the blue, and is not explained. (4) "In a recurring theme...". I have no idea what the authors are alluding to. (5) "...the non-ideality of the off-diagonal element". Another unnecessary obscurity. (6) "f" in many equations. This is a fraction, but whether mole or mass fraction I don't think is explained, though the authors appear to decide that the "appropriate" one is close to a volume fraction (end of section 3.3, and a long time after it is first introduced). I did not get all the way through the theory section. In my opinion the authors are so deeply involved in the development of their theory that they have been unable to explain it clearly, simply, and methodically to potential users. There are too many leaps of faith, and too much obscure language and unclear writing for me to be convinced. There may be a good paper here, but it will require substantial re-writing to produce it.

As we mention above, we have substantially re-written the paper.

There is one other point about presentation: papers should be written so that diagrams, and their description, should be understandable from a black and white printout. The authors make rather indiscriminate (and unnecessary) use of colour, and refer to colours explicitly in the text.

If this were true then the use of color in publications would be completely gratuitous. It is indeed much harder to read these figures in black and white, but we agree that it is best to try to make the figures as readable as possible. Wherever we can, we have made sure to identify shape in addition to color (green triangle, etc). However, in the end we used color because we believe it makes the figures easier to read – it follows that not using color makes them more difficult to read.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 24091, 2010.

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