Atmos. Chem. Phys. Discuss., 10, C3843–C3845, 2010
www.atmos-chem-phys-discuss.net/10/C3843/2010/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Technical note: Vapor pressure estimation methods applied to secondary organic aerosol constituents from α-pinene oxidation: an intercomparison study" *by* S. Compernolle et al.

Anonymous Referee #2

Received and published: 11 June 2010

General Comments

After reviewing the manuscript the conclusion is that it is suitable for publication in the journal after minor modifications.

The work is dealing with the estimation of pure component vapor pressure data for components appearing in the BOREAM model, which describes the detailed reaction path of alpha-pinene oxidation.

Various estimation methods were applied to the components and partly extended by

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

regressing new group contribution values. The differences between the models are discussed in detail. During the test a deficiency in one of the models became apparent: Group contribution usually implies additivity of the influence of the structural groups on a physical property. In case of hydrogen-bonding groups, competitive association leads to non-additivity as can easily be verified when looking at simple alcohols and glycols. The methods of Nannoolal and Moller contain a so called interaction term that is supposed to correct this effect. In contrast to the methods of Nannoolal et al, Moller had changed the equation for this "interaction contribution" leading to unrealistic results for higher numbers of associating groups.

The method has meanwhile be overworked by Moller et al. based on this analysis and a correction will be published shortly.

The drawback of this work and other comparable research lies in the very limited amount of basic experimental data in literature.

Specific Comments:

1) 1 - Introduction, line 11-16 When discussing the use of corrections for non-additivity, the authors should remark that methods which lack such a feature are in principle unable to correctly describe the vapor pressure of components with more than one hydrogen-bonding group. While this correction requires more parameters to be regressed, it is nevertheless important.

2) 2 – Description. . ., line 16-18 The Joback method should in principle only be applied to components within a certain boiling point range. Nevertheless, when used outside this range, a correction can be applied that can simply be derived from a plot of estimated vs. experimental normal boiling temperature for a sufficient number of components.

3) 2.2 Boiling . . .., line 13 blank missing: Data Bank hypenation: para-meter

4) 5 Conclusions, line 7ff It may seem a drawback to first estimate a normal boiling

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

temperature and then calculate the vapor pressure value at a much lower temperature but this should also be viewed from the perspective of physical significance of the estimated properties. At the normal boiling temperature a certain ratio exists between the molecular interaction and the thermal energy while the entropy of vaporization only changes slightly and in a simple way with temperature. The normal boiling point correlates to some extend with the slope of the vapor pressure curve but this correlation is not strict enough. Group contribution parameters that can describe the boiling temperature do not correlate well with those describing the slope. Generally estimation of vapor pressure at a given temperature is therefore much more difficult than estimation of a boiling temperature for a given pressure as it would require describing separate phenomena with one set of parameters.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 8487, 2010.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper