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Atmospheric
Chemistry
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Discussions

Interactive comment on “Effects of uncertainties in the thermodynamic properties of aerosol components in an air quality model – Part II: Predictions of the vapour pressures of organic compounds” *by* S. L. Clegg et al.

Anonymous Referee #1

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The paper deals with the effect of uncertainties in thermodynamic models on the results of an air quality model (UCD-CACM model) by Griffin, Kleeman and co-workers. This work presents a very carefully conducted research and is well presented. Comments and additions given in this review reflect mostly conform to the findings of the authors and are meant to add further details about the basis and limitations of the different methods for future work in the field of atmospheric chemistry.

The UCD-CACM model requires knowledge about the pure component vapor pressure and Henry coefficients in water of a large number of components for which usually no experimental data are available.

Henry coefficients can be conveniently calculated from the product of the activity coefficient at infinite dilution in water and the pure component vapor pressure.

Due to the high dilution of the solutes in the aqueous aerosol phase, the activity coefficient can deviate very far from unity. In case of hydrocarbons, values larger than 10^5 can be observed.

For the estimation of these values the UNIFAC model is employed.

It should be mentioned that this model was only regressed to VLE data and leads to rather large deviations in case of activity coefficients at infinite dilution. Modifications of UNIFAC were developed by Fredenslund et al. from Lyngby, Denmark and Gmehling et al. from Dortmund and Oldenburg in Germany. The Lyngby version was discontinued after one publication in 1983 (at least no further parameters were published) while mod. UNIFAC (Dortmund) is still being further developed until today and parameters are regressed to a variety of mixture data including activity coefficients at infinite dilution.

Due to limited funding (further improving the model is usually not considered new science) this work had to switch to private funding around 1995 and only a limited amount of new parameters is published. Further information is available at www.unifac.org. .

For F-Cl-compounds, a special refrigerant-submatrix should be used (http://134.106.215.86/UNIFAC/Mod.%20UNIFAC%20Refrigerant.htm).

In case of alkanes or alkenes in water it is very important to apply a correction to the UNIFAC or mod. UNIFAC results as these values are greatly underestimated. The following Figure shows experimental vs. calculated water solubilities in mol/dm^3. The saturated mole fraction in case of broad miscibility gaps is very close to the reciprocal activity coefficient at infinite dilution.

See Figure 1.

In addition it should be noted that activity coefficients at infinite dilution of unpolar components in water are significantly increased by addition of electrolytes (salting out effect).

In order to reduce the number of different components, the UCD-CACM model employs a number of so called primary and secondary surrogate compounds.

As only very few vapor pressure data are available for these components, the authors chose to compare the results of different estimation methods in order to identify the range of uncertainty.

As vapor pressures around ambient temperature are required, both estimates of the normal boiling temperature and the temperature dependence of the vapor pressure via ΔS_b and $\Delta C_p^{(gl)}$ or ΔH_b are required in case the model only estimates the normal boiling point. These can for example be estimated by the method of Myrdal and Yalkowsky. Other methods employed contain their own estimation procedures for the temperature dependence of the vapor pressure.

The methods examined in this paper cover those of

- Nannoolal et al., 2004
- Cordes and Rarey, 2002
- Wen and Qiang, 2002
- Marrero-Morejon and Pardillo-Fontdevila, 1999
- Stein and Brown, 1994
- Constantinou and Gani, 1994
- Joback and Reid, 1987

- Advanced Chemistry Developments (Kolovanov and Petrauskas, undated)

which are all based on molecular structure.

The authors discuss the results of the different estimation methods. Their findings are generally in agreement with my own experiences during the test of available methods and development of new correlations.

They give a brief and generally correct description of the individual methods but a few remarks should be added:

Joback and Reid (1987) correlated the normal boiling point, Tb, of organic compounds containing the elements C, H, O, N, S and the halogens according to: Tb = 198.2 + Σ i nigi where gi (equal to Δ Tb(i)) is the increment value of group i and ni is the number of times the group occurs in the compound.

As stated here, Joback and Reid employ a linear relationship between the sum of group contribution and the normal boiling point. This linear relationship is only valid over a certain range of molecular size or boiling point. Within this range, the method yields reliable results except for multifunctional compounds but it should not be applied to large molecules with high boiling points. The following figure shows results from different methods for n-alkanes and n-alkanols:

See Figure 2.

Hydrogen bonding functional groups usually do not observe the additivity assumed in group contribution methods. The following Figure from the work of Nannoolal et al. shows results for some families of multifunctional compounds:

See Figure 3.

Without a special parameter to correct the non-additivity, all models give very erroneous results. Models that do not take into account this non-additivity should not be applied to multifunctional compounds.

The ACD-method by Kolovanov and Petrauskas yields astonishingly good results but the exact estimation procedure used in this commercial method was never published.

In a previous review of prediction methods for boiling points (J.C. Dearden, Env.Toxicol.Chem. Vol.22, 1696, 2003) Dearden had tested various prediction programs (using 100 common components only) and claims that ACD (www.acdlabs.com) can predict normal boiling points with an absolute average deviation of 1 K.

As this deviation is unrealistically small, we examined the ACD website for a possible clue and found:

“To determine constants and relationships, our algorithm uses an internal database that contains boiling points for 10,000 compounds - 6,000 of which have boiling point values at 760 mmHg. The database values were also used to evaluate and fine-tune the specialized algorithms for ACD/Boiling Point. Your compound does not have to be in the database in order to have its boiling point calculated.”

If the component to be estimated conforms to one of the macro-fragments (10 000 components) available to the program, probably the experimental value for this macro-fragment is used directly - i.e. the estimation result would be the normal boiling point stored in their database. A true test of the ACD program should therefore be based on data for components that are definitely not in the large internal database of the software or very similar to components included.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 11049, 2007.

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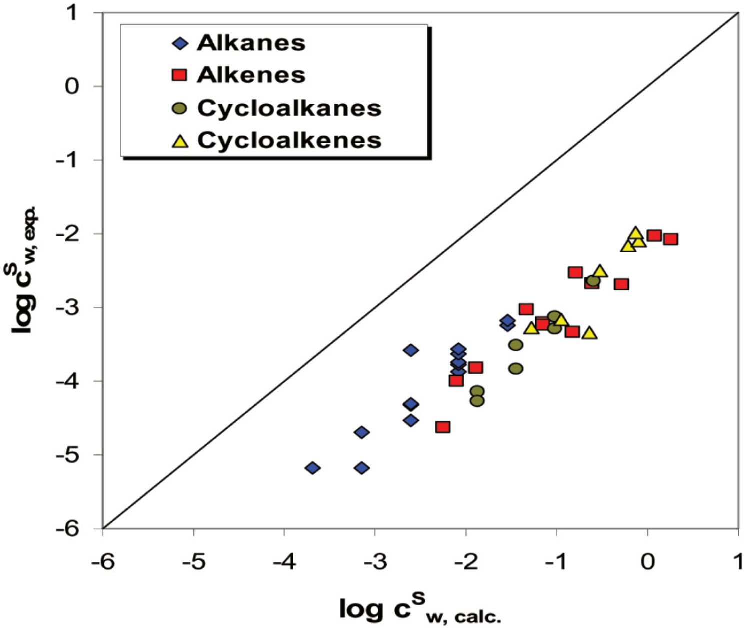
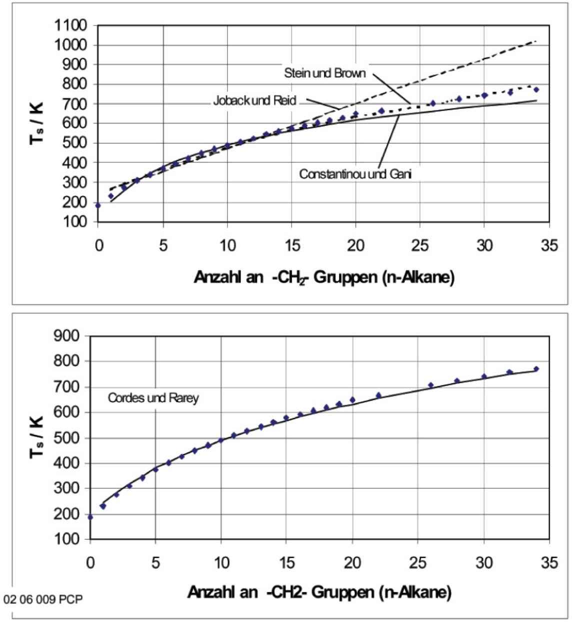

◆ Alkanes
■ Alkenes
● Cycloalkanes
△ Cycloalkenes
1
0
-1
-2
-3
-4
-5
-6
$\log c^{S}_{w,\,exp.}$
-6
-5
-4
-3
-2
-1
0
1
$\log c^{S}_{w,\,calc.}$

Figure 1:



Joback und Reid, Stein and Brown

$T_s = A + \Sigma\, N_I{*}C_I \qquad [T_s = f_{corr}(T_s)]$

Constantinou and Gani

$T_s = 204.359 \ln(\Sigma\, N_I{*}C_I + \Sigma\, M_I{*}D_I)$

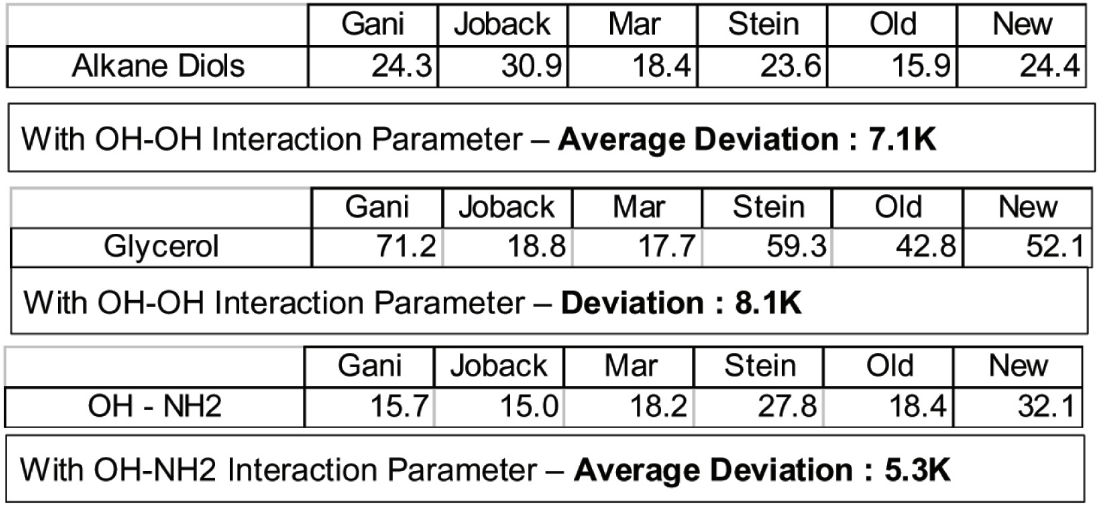
N_I - number of first order groups type i
C_I - group contribution of first order group i
M_I - number of second order groups type i
D_I – group contribution of second order group i

Cordes und Rarey, Rarey and Nannoolal

$T_s = (\Sigma\, N_I{*}C_I) / (n^a + b) + c$

a,b,c - adjustable parameters
N_I - number of first order groups type i
C_I –group contribution of first order group i
n - number of atoms except carbon

Figure 2:



	Gani	Joback	Mar	Stein	Old	New
Alkane Diols	24.3	30.9	18.4	23.6	15.9	24.4

With OH-OH Interaction Parameter – **Average Deviation : 7.1K**

	Gani	Joback	Mar	Stein	Old	New
Glycerol	71.2	18.8	17.7	59.3	42.8	52.1

With OH-OH Interaction Parameter – **Deviation : 8.1K**

	Gani	Joback	Mar	Stein	Old	New
OH - NH2	15.7	15.0	18.2	27.8	18.4	32.1

With OH-NH2 Interaction Parameter – **Average Deviation : 5.3K**

Figure 3:

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