

## ***Interactive comment on “Henry’s law constants of polyols” by S. Compernelle and J.-F. Müller***

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### **1 Reply to reviewer 1**

We like to thank reviewer #1 for the careful review and comments. The suggestions and corrections provided helped us to improve the article. They are discussed point-by-point below.

#### 1.1 General comments

**Reviewer #1.** One point worth clarification concerns the sensitivity test calculations with aqueous ammonium sulphate aerosol solutions described in Section 5 and impli-

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cations of this discussed in Section 6. I suggest to mention that the gas-liquid partitioning described with Henry’s law actually applies to the limiting case of an organic compound being present in tiny amounts (both in gas and liquid phases) only, as defined by Eq. (1). This may therefore not apply to all situations found in the lower atmosphere. In addition, as soon as not only an aqueous ammonium sulphate phase is present in an aerosol, but, e.g., also a hydrophobic organic phase, the partitioning of the considered polyols may be quite different from the simple examples given in the calculations and shown in Figure 2; see, e.g., Zuend et al. (2010). In such a case, less hydrophilic compounds may still partition substantially to the particles, despite the simple Henry’s law calculation (and activity coefficient values in the aqueous phase) suggesting otherwise.

**Author’s response.** We added clarifications in Section 5 and 6 based on the reviewer’s comments.

Section 5, page 13539, line 20, we add:

“We note that this discussion, based on Henry’s law, is only applicable if the organic compound is present in a tiny amount, and this may not be justified for all situations encountered in the lower atmosphere.”

Section 5.2, page 13540, line 22, we add:

“Note however that this test is only applicable to a situation with a tiny amount of organics. If e.g. a separate organic phase is present, less hydrophilic compounds may partition substantially to the particles, even if the HLC based analysis suggests otherwise.”

Section 6.3, page 13546, line 15, we add:

“Note that this analysis is only applicable for aqueous AS aerosol in the limiting case of small concentration of organics. If e.g. a separate organic phase is present in the aerosol, partitioning to this phase should be taken into account as well.”

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## 1.2 Specific comments

**Reviewer #1.** p. 13530, line 23: “enthalpy of gas phase dissolution”, perhaps better: enthalpy of dissolution of a gas phase species. Check also the subscripts in the formula given there.

**Author’s response.** Replacement done and subscripts corrected here, as well as on the first line of 13531.

**Reviewer #1.** p. 13532, line 6: “its liquid vapour pressure”; better: its pure liquid-state vapour pressure.

**Author’s response.** “liquid vapour pressure” replaced with “pure liquid state vapour pressure”

**Reviewer #1.** p. 13532, line 7: “corresponding enthalpy change”; unclear: state what process is meant.

**Author’s response.** Replaced by “the enthalpy of dissolution of an infinitesimal amount of gas phase species”. Also p. 13533 “enthalpy change” is replaced by “enthalpy of dissolution of gas phase species”

**Reviewer #1.** p. 13532, line 15: “liquid, at infinite dilution”; change to: liquid solute at infinite dilution.

**Author’s response.** Replacement done.

**Reviewer #1.** p. 13532, 13533., Eq. (5) vs. Eq. (10): Check the equations regarding factor R.

**Author’s response.** We apologize for this oversight. In Eqs. (5), (6), (7), (11) and (12) the factor  $R$  has been added at the appropriate places.

**Reviewer #1.** p. 13535, line 21: “due to the crystal contribution”; this is vague, please clarify what is meant.

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**Author’s response.** Replaced by: “as this depends on the molecular arrangement in the crystal structure which is compound-specific.”

**Reviewer #1.** p. 13535, line 22: I suggest to write there “liquid state vapour pressure”.

**Author’s response.** Replacement done. The same is done at p. 13535, line 18.

**Reviewer #1.** p. 13536, Eq. (17): Check the subscripts “g” of  $C_{p,g}$  in the integrals related to the entropy/enthalpy changes of the fusion phase transition. Shouldn’t it be  $C_{p,L} - C_{p,Cr}$  ?

**Author’s response.** We derive Eq. (17) here for  $\Delta S_{sub}(T_{ref})$  step-by-step

$$\Delta S_{sub}(T_{ref}) = S_g(T_{ref}) - S_{Cr}(T_{ref}) \quad (1)$$

$$S_g(T_{ref}) = S_g(T_{meas}) + \int_{T_{meas}}^{T_{ref}} \frac{C_{p,g}}{T} dT = S_g(T_{meas}) + \int_{T_{meas}}^{T_{fus}} \frac{C_{p,g}}{T} dT + \int_{T_{fus}}^{T_{ref}} \frac{C_{p,g}}{T} dT \quad (2)$$

$$S_{Cr}(T_{ref}) = S_{Cr}(T_{fus}) + \int_{T_{fus}}^{T_{ref}} \frac{C_{p,Cr}}{T} dT \quad (3)$$

$$S_{Cr}(T_{fus}) = S_L(T_{fus}) - \Delta S_{fus}(T_{fus}) \quad (4)$$

$$S_L(T_{fus}) = S_L(T_{meas}) + \int_{T_{meas}}^{T_{fus}} \frac{C_{p,L}}{T} dT \quad (5)$$

Substituting the RHS of Eq. (5) in Eq. (4), then the RHS of Eq. (4) in Eq. (3), and finally the RHS of both (2) and (3) in (1), Eq. (17) of the article is correctly obtained. The same procedure holds for  $\Delta H_{sub}(T_{ref})$ .

**Reviewer #1.** p. 13536, line 17: Replace “solid state pressures” by “solid state vapour pressures” (for clarity, since the vapour pressure is meant, not the pressure of/in a solid).

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**Author's response.** We adapted this here, as well as at p. 13530, lines 5 and 25, p. 13535, lines 17 and 20 and at other occurrences.

**Reviewer #1.** p. 13542, line 11: "Note that AS has a deliquescence RH (DRH) of 79.5% and an efflorescence RH (ERH) of ~35% (Martin, 2000)." For clarity, write: "Note that pure AS particles have a ...", since this is not necessarily true when other components are present (besides AS and water).

**Author's response.** Sentence adapted.

**Reviewer #1.** Following sentence: "Below the ERH, only solid AS is present in the particulate phase." could be misunderstood, since also below the DRH only solid AS may be present or otherwise a liquid, supersaturated solution, depending on the RH history of a particle (i.e., if previously dried below ERH or not). DRH is the stable equilibrium point (referring to the solubility limit of solute).

**Author's response.** We modified the sentence into:

"The DRH is the equilibrium point below which solid AS is the thermodynamically stable phase and this corresponds to the solubility limit of AS in water. However, depending on the RH history of the particle, a metastable supersaturated solution may instead be present below the DRH. Below the ERH, only solid AS is present in the particulate phase."

**Reviewer #1.** p. 13543, Eq. (25): As done in Eq. (2), Eq. (25) refers to the limiting case of pressure and mole fraction  $\rightarrow 0$ . Therefore, state the limits in the expression.

**Author's response.** This is done.

**Reviewer #1.** p. 13546, line 6: "diols will be partially or completely in the aqueous phase in clouds,;" should it read "gas phase" instead of "aqueous phase" here?

**Author's response.** No, aqueous phase is meant. For example, 1,4-butane diol will be completely in the aqueous phase as its  $k_h$  of  $3.5 \times 10^6$  M/atm is larger than the upper

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limit of  $k^*$ . 1,2-hexane diol has a  $k_h$  of  $1.7 \times 10^5$  M/atm which is in the range that  $k^*$  can take. To be more clear, we changed the sentence into:

"According to the HLC derived in this and the previous work (Compernelle and Müller, 2014), diols will be partially (e.g. 1,2 hexane diol, depending on the droplet size) or completely (e.g. ~1,4-butane diol) in the aqueous phase in clouds, ..."

**Reviewer #1.** Table 2: The pressure unit of atm is used, which is an obsolete unit. Atmos. Chem. Phys. asks authors to use SI units whenever possible, thus, use Pa (or kPa) for tabulated data. The same applies to Table 4.

**Author's response.** In Table 2, we have converted the units to Pa. Regarding Table 4 however, we prefer to keep the 'M/atm' unit for Henry's law constant, as it is more commonly used than the SI unit (Sander, 1999), and to keep consistency with our previous work (Compernelle and Müller, 2014) and the compilation of Sander (1999).

**Reviewer #1.** Table 4: State the temperature for which the quantities are listed.

**Author's response.** "at 298.15 K" added in the caption.

### 1.3 Technical corrections

**Reviewer #1.**

- p. 13534, line 17: delete "(see Eq. 13)".
- p. 13540, Eq. (20): RT should be math mode (RT).

**Author's response.** The technical corrections have been implemented.

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## 2 Reply to reviewer 2

### 2.1 General Comments

**Reviewer #2.** The authors report the calculation of Henry's law constants (HLC) for several polyols from literature data for water activity and vapour pressure and calculated/ estimated data for infinite dilution activity coefficients (IDACs), sublimation vapour pressures and activity coefficient ratios. These HLC values and those from a previous work are used to assess the partitioning of polyols, diacids and hydroxyacids into aqueous aerosol. The paper would be improved by a more detailed description of how exactly the authors did their calculations and more analysis of the effect of errors in their input values on the HLC values they calculate. This reviewer recommends that this paper is published in Atmospheric Chemistry and Physics after the following issues have been resolved.

**Author's response.** We thank the reviewer for the many suggestions to improve the manuscript. We include now more detail about the calculations, also including more references. A detailed error analysis concerning all relevant quantities is now included in an appendix.

### 2.2 Specific Comments

**Reviewer #2.** Introduction:-In their previous paper (Compernelle and Muller 2014) the authors provide an excellent critique of the available 'experimental' HLC values for diacids and hydroxyl polyacids from the literature. Although the data for these polyols is much more limited than that for the polyacids, it would be a useful addition to the introduction if the authors could summarise and critique the literature data for HLC values for polyols in this paper in a similar way.

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**Author's response.** To provide more context, we add now a short paragraph:

"HLC data on polyols is limited. Data is available e.g. in the often-cited compilation of Sander (1999). In this compilation however, most values are estimated by a group-contribution method, while only for three molecules experimental values are included, and some of the data was evaluated as unreliable."

**Reviewer #2.** p. 13531-line 6:- References needed for E-AIM

**Author's response.** We changed the sentence into:

"... making use of a model presented at the site E-AIM (Extended AIM Aerosol Thermodynamics Model), available at <http://www.aim.env.uea.ac.uk/aim/aim.php>, (see e.g. Clegg and Seinfeld; Friese and Ebel, 2010) to calculate the acid dissociation."

**Reviewer #2.** p. 13531-Eq. 2:- what is the significance of the superscript 'px'? What is its meaning?

**Author's response.** The 'px' subscript was introduced by Sander (1999) (to which we refer) to specify that vapour pressure  $p$  is used for the gas phase concentration, and mole fraction  $x$  for the aqueous phase concentration. This is now specified in the text:

"The  $px$  superscript specifies that vapour pressure  $p$  is used for the gas phase concentration, and mole fraction  $x$  for the aqueous phase concentration."

**Reviewer #2.** p. 13531-line 23:- Might be helpful to remind the reader  $C_w = 55.5$  Moles/Litre.

**Author's response.** We appended "(equal to 55.5 mol/L at 298.15 K)"

**Reviewer #2.** p. 13532- Eq 5-7:- A reference for this use of the Van't Hoff equation is required.

**Author's response.** We inserted a reference to the handbook of Atkins and de Paula (2006).

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**Reviewer #2.** p. 13532-Eq 5. An 'R' is missing from in front of the derivative.

**Author's response.** This has been inserted. Likewise for equations (6), (7), (11) and (12).

**Reviewer #2.** p. 13532-Eq 8. A reference is required for the derivation of this equation?

**Author's response.** A reference to our previous paper (Compernelle and Muller 2014), where this equation is derived, is included.

**Reviewer #2.** p. 13533-Eq 10-12. A reference is required for the derivation of these equations.

**Author's response.** References and some extra explanation is provided:

“Eq. (11) is the Clausius-Clapeyron equation for sublimation (Atkins and de Paula, 2006). Eq. (12) can be derived by combining Eqs. (8), (6) and the van't Hoff relation for the activity of the solid (see e.g. Nordström and Rasmuson, 2008) “

**Reviewer #2.** p. 13534 line 1:- Methods to estimate activity coefficients considerably pre-date the references quoted here. The original paper defining UNIFAC (Fredenslund et al. 1975) should be included in this set of references.

**Author's response.** This reference is included.

**Reviewer #2.** p. 13534-Section 3.1:- lines 3 to end of page:- The authors need to clarify how exactly they derived their values for IDAC and the activity coefficient ratio as discussed in Section 3.3.

In its present form this section is very confusing. Eq. 13 is an integral form of the Gibbs-Duhem relationship which can provide an IDAC for the solute. Did the authors use Eq. 13 to get the IDAC values for any of their compounds (if the methods given in Appendix A in Compernelle and Muller 2014 were followed then probably not)? Activity coefficient expressions such as Margules, Van Laar, Wilson, or UNIQUAC obey the Gibbs-Duhem relationship (ie. Eq 13) and, once the relevant parameters have been

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fitted to the data, the IDAC value can be obtained directly. Is there an advantage to using Eq 13 to get the IDAC values rather than fitting the available  $a_w$  data to (say) the Margules equation and obtaining the IDAC values from the Margules equation directly? Do the authors combine an activity coefficient expression with Eq. 13 in some way to get the IDAC values? In which case they should explain in more detail how they do this. If the authors do not use Eq. 13 to calculate IDAC values then perhaps it should be removed to avoid confusion. Either way the authors should make it much clearer how they calculated their IDAC values. If Eq. 13 is retained then Mansoori 1980 should be quoted as a reference (as this provides the derivation) and the authors should provide an explanation of what 't' is. If an activity coefficient expression was used to calculate the IDAC values then which equation was used for each compound should be provided either in this section or in Table 1. Also Table 1 should include some information about the composition range of the data that was fitting to the activity coefficient expression.

Also the use and validity of Eq. 14 is unclear. Do the authors have a reference or any other evidence that this equation is valid? The whole point of using something like the Margules equation (or Eq. 13) is that the same equation (with the same fitted parameters) is used across the whole composition range to ensure that Gibbs-Duhem is obeyed. If the authors use one equation for part of the composition range and a different equation for the rest then Gibbs-Duhem will not be satisfied. However fitting one set of data to one equation and a second set to a different equation would be fine (using different Margules parameters which would give two different IDAC values- as seen in Table 1) so is Eq 14 really describing the method used by the authors to fit two or more sets of data for the same organic solute?

**Author's response.** We tried to be concise in our description; we regret if this led to confusion. We removed some explanation from Section 3.1 (e.g. Eq. (14) and its discussion). Instead, we inserted now a more detailed explanation in the Appendix. It is integrated in the error analysis, as the derived uncertainty in IDAC depends on the  $a_w$  data and how these are used. We prefer to keep the Gibbs-Duhem Equation

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(Eq. 13) as it is generally valid, both if the integral is solved numerically or analytically, while e.g. the Margules equation has a more limited scope. Instead of  $t$  we use now  $x_w$  as integration variable, to improve clarity. The reference to Mansoori (1980) is included. The activity coefficient expressions (Margules, Van Laar, etc.) are given in the Appendix, and also the specific parameterisations. The composition range is not included per experiment, but described in the appendix in a general way: mole fraction of 0.1-0.95 for the Marcolli data, 0.93-0.996 for the other data.

Regarding the reservations that the reviewer has about Eq. (14). Let us restate here the integral form of the Gibbs-Duhem equation (e.g. Mansoori, 1980).

$$\ln \gamma_s^\infty = \int_0^1 \frac{\ln \gamma_w(x_w)}{(1-x_w)^2} dx_w$$

If sufficient fine-grained data would be available over the whole composition range, it would be most straight-forward to solve the integral numerically. However, this is not the case here. An alternative is to fit the  $\ln \gamma_w$  data with a function  $f(x_w)$ , and then applying the integration on this function. If  $f(x_w)$  is e.g. a Margules expression the integration is well known and  $\ln \gamma_s^\infty$  can be directly evaluated from the fitting parameters of  $f(x_w)$ , but in general  $f(t)$  could be an arbitrary function; it should merely provide a good fit to the  $\ln \gamma_w$  data. In many cases, a single activity expression (Margules, Van Laar,...) was enough to fit all data.

It is of course true that

$$\int_0^1 \frac{f(x_w)}{(1-x_w)^2} dx_w = \int_0^{\tilde{x}_w} \frac{f(x_w)}{(1-x_w)^2} dx_w + \int_{\tilde{x}_w}^1 \frac{f(x_w)}{(1-x_w)^2} dx_w$$

Suppose now that none of the activity expressions we use can give a good fit of all  $\ln \gamma_w$  data over the entire range. However, as  $f(x_w)$  can be a general function, there is nothing that prevents us from defining

$$f(x_w) = f^{(1)}(x_w) \text{ if } t < \tilde{x}_w$$

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$$f(x_w) = f^{(2)}(x_w) \text{ if } t > \tilde{x}_w$$

with  $f^{(1)}(x_w), f^{(2)}(x_w)$  different  $\ln \gamma$  expressions. This leads us to Eq. (14):  $\ln \gamma_s^\infty = \int_0^{\tilde{x}_w} \frac{f^{(1)}(x_w)}{(1-x_w)^2} dx_w + \int_{\tilde{x}_w}^1 \frac{f^{(2)}(x_w)}{(1-x_w)^2} dx_w$  Of course if e.g.  $f^{(1)}$  is a Margules expression and  $f^{(2)}$  is a Van Laar expression, then the parameters of either expression do not correspond directly to  $\ln \gamma_s^\infty$ . But that does not prevent us from evaluating both integrals.

We hope this makes clear the approach we followed. As noted above, we've put now a more detailed explanation in the Appendix.

**Reviewer #2.** p. 13535 line 5-9:- Using two sets of data to get two different IDAC values for the smaller diols gives an idea of the sensitivity of the IDAC values to errors in the aw data. However, as the authors correctly point out, as the IDAC values increase for the more hydrophobic diols the uncertainty will be larger and for some of these diols there is only one value for IDAC because there is a single set of aw data. It might be suspected for (say) 1,7 heptane diol or 1,2 hexane diol, that any fitted parameters in an activity coefficient expression may be poorly constrained and consequently the IDAC values sensitive to small errors in aw. Could the authors do a sensitivity analysis using one of the above compounds and applying- 1) a small random error (do the authors providing the experimental data quote an error for their aw values?), and 2) a small systematic error to the aw data to see what effect this has on the calculated IDAC value.

**Author's response.** This is a good suggestion. In the newly-included error analysis in the appendix, systematic and random errors are applied to the  $a_w$  data and the impact on IDAC investigated. Moreover, also the impact of choice of the fitting function is analysed.

**Reviewer #2.** p. 13535 line 25 to p. 13536 line 10:- Equations 15-17 need a reference. Also it might help to make your nomenclature in these equations clearer if you state that  $\Delta S_{\text{sub}}$  and  $\Delta H_{\text{sub}}$  are weak functions of temperature.

**Author's response.** The temperature correction is now stated as Kirchhoff's law, with a reference to Atkins and de Paula (2006). "with  $\Delta H_{\text{sub}}$  and  $\Delta S_{\text{sub}}$  weak functions of temperature" is added after Eq. (16).

**Reviewer #2.** p. 13537:- Discussion of the results for sublimation pressures.

p. 13537 lines 1-2:- The authors should provide some figures about the agreement for fusion data between different data sources (were they all within 5% of each other or 3% or 1%?).

**Author's response.** Comparison of fusion data of the polyols with 4 or more OH groups is now included in a paragraph. Also an error analysis regarding the impact of uncertainty in fusion data on  $k_h$  is included in the Appendix.

**Reviewer #2.** The authors make a convincing case that the integrals involving the heat capacity integrals are important to the calculation of  $p_{\text{Cr}}^0$  but they have nothing to say about the effect of error in the heat capacity values and the  $\Delta H/\Delta S$  values in Eq. 16 and 17 on the calculation of  $p_{\text{Cr}}^0$ . The authors should do a sensitivity calculation for some of the compounds in Table 2 (in particular for sorbitol or mannitol where the extrapolation is large) where the effect of (say) a 5% error (or if the data suggests a more representative estimate of the error use that) in heat capacity values and the  $\Delta H/\Delta S$  values and its impact on  $p_{\text{Cr}}^0$  can be evaluated. From this the authors should be able to draw some conclusions about the relative importance of errors in these quantities and how this varies with the temperature difference ( $T_{\text{meas}} - T_{\text{ref}}$ ).

**Author's response.** In the error analysis in the appendix, uncertainties on  $p_{\text{Cr}}^0$  are derived based on an intercomparison of  $p^0, \Delta H_{\text{vap/sub}}, C_p, T_{\text{fus}}$  and  $\Delta H_{\text{fus}}$  between different data sources, and a sensitivity test is performed based on this. We also investigated the impact of stereo-chemistry on  $C_{p,L}$  and  $C_{p,Cr}$  (as in some cases we had to use  $C_p$  of a stereo-isomer) and tried to quantify the error on  $C_{p,g}$  (made difficult because this quantity is estimated). For this intercomparison exercise, new data is included, e.g. from Lopes Jesus et al. (2005); Parks and Huffman (1926); Parks and Anderson

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(1926). As can be expected, for a large ( $T_{\text{meas}} - T_{\text{ref}}$ ) difference the error is the largest.

**Reviewer #2.** The authors should include  $T_{\text{fus}}$  values in Table 2 and also, rather than a single point for  $T_{\text{meas}}$ , they should indicate the temperature range of the data which they have used to derive their  $\Delta H_{\text{sub}}$  and  $\Delta H_{\text{vap}}$  at  $T_{\text{meas}}$ .

**Author's response.** In Table 2, we have replaced  $T_{\text{meas}}$  with the temperature range. The  $T_{\text{fus}}$  values we did not include in this Table, but in a Table in the error analysis section in the Appendix.

**Reviewer #2.** p. 13537 line 21-22:- 'The high temperature  $p_L^0$  and  $p_{\text{Cr}}^0$  data of erythritol and pentaerythritol is comparable among the data sources. . . ' this is too vague. In what way are these three sets of data comparable [...]?

**Author's response.**

To clarify this, we added the following part to the sentence:

"; if the  $p^0$  parameterisations presented in these works are evaluated at mid-points between their respective  $T_{\text{meas}}$ , differences ranging from 4% up to 40% are obtained."

**Reviewer #2.** [...] and if they are so similar why do they give different  $\Delta H_{\text{vap}}$  or  $\Delta H_{\text{sub}}$  and different estimates for  $p_{\text{Cr}}^0$  at 298.15K? Doesn't this highlight one of the difficulties with this method (as defined by equations 15-17) of deriving sublimation pressures at 298.15K from high temperature vapour pressure data. The high temperature data needs to be very accurate and over a substantial temperature range to provide an accurate slope of the vapour (or sublimation) pressure. [...]

**Author's response.** It is true that the uncertainty in  $\Delta H_{\text{vap}}$  or  $\Delta H_{\text{sub}}$  dominates the error in  $p_{\text{Cr}}^0$  at 298.15K (and also in  $k_h$ ), at least for the polyols with 4 or more hydroxyl groups. This is now shown in the error analysis in the Appendix, and discussed in Section 6.1. However, one must also take into account that the old studies of Nitta (1950, 1951) and Bradley (1953) were done over a smaller temperature interval, and for much less data points, compared to the Barone (1990) study. Therefore, we think

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the slopes of Nitta and Bradley are less reliable, and their data is not retained for the final  $k_h$  calculation.

**Reviewer #2.** [...]. The authors should discuss the limitations and advantages of their method against alternative methods for calculating values for  $p_{Cr}^0$ . For example it is known that for some vapour pressure estimation methods that require normal boiling point ( $T_b$ ) as an input (eg. Nannoolal et al. 2008) the vapour pressure correlation is relatively accurate and most of the error (for low volatility compounds) comes from the estimation of  $T_b$ .

Hence an alternative method to obtain  $p_{Cr}^0$  would be to use one of the standard vapour pressure estimation methods; fix the boiling point to give the experimental vapour pressure or sublimation pressure at  $T_{meas}$ ; and estimate the subcooled liquid vapour pressure at 298.15K which can then be converted to the crystal sublimation pressure using the equation for the ratio of the solid/supercooled liquid fugacities (Prausnitz et al 1986), with the simplification that the gas phase is ideal and  $T_{fus}$  is a good approximation to the triple point temperature). This is the same equation as Eq. 1 in Compernelle et al., 2011.

**Author's response.**

We have reservations concerning this alternative approach proposed by the reviewer. While the Nannoolal et al. (2008) vapour pressure method (and similarly, the Moller et al. (2008) vapour pressure method) are successful especially for monofunctional compounds, there can be issues for highly polyfunctional compounds. From the theses describing the development of both methods (Nannoolal, 2006; Moller, 2007, p. 127), it is clear that only compounds were considered where a normal boiling point is available. This excludes the polyols with 4 or more OH groups. Therefore, these methods may not be well-suited to calculate the vapour pressure of these kind of compounds. In fact, the original version of the Moller method contained a bug that we pointed out (Compernelle et al., 2010), showing up only for highly polyfunctional compounds, and

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giving very unrealistic values. While this bug has been corrected since then, it does indicate that the method was not devised for highly polyfunctional compounds.

We did some test calculations using the vapour pressure estimation methods available on-line at the site of E-AIM (<http://www.aim.env.uea.ac.uk/aim/aim.php>) for the polyols with 4 or more hydroxyl groups. The three methods provided (Nannoolal et al., 2008; Moller et al., 2008; Myrdal and Yalkowsky, 1997) all calculate  $p_L^0$  and require a normal boiling point  $T_b$  as input. As suggested by the reviewer, we adjusted  $T_b$  until the high-temperature data of  $p_L^0$  Barone et al. (1990) could be reproduced. Then, the  $p_L^0$  (298.15K) was calculated using this boiling point. The results are given in a separate appendix. The method of Myrdal and Yalkowsky (1997) gave much higher  $p_L^0$  (298.15K) than the other two methods, e.g. for sorbitol it was higher by a factor 200–400. The final  $p_L^0$  (298.15K) result of the Nannoolal method and of the Moller method are in closer agreement (e.g. for sorbitol within a factor 2), however, the  $T_b$  value that had to be used was very different (for sorbitol: 674 K for the Nannoolal method, 789 K for the Moller method). This also points to problems with this methodology.

**Reviewer #2.** p. 13538:- Section 3.3:- Similar issues to those raised in Section 3.1. Do the authors need to quote Eq. 18? Was it used to calculate the ratio of the activity coefficients? If not should it be removed to avoid confusion to the reader? From figure 1 and the text in this section it is clear that the  $a_w$  data was correlated using the Margules equation. The form of the Margules equation should be provided, either in this section, or in Section 3.1. If Eq. 18 is to be retained can the derivation of Eq. 18 from Eq. 10 in Compernelle and Muller 2014 be provided (perhaps in an Appendix).

**Author's response.** The Margules equation (along with other activity coefficient expressions) is now presented in the Appendix. To be more explicit on how we derived the activity coefficient ratios, we include now in the text:

“The precise procedure is described in Appendix A of Compernelle and Muller (2014) and the resulting parameters are shown in Fig. 1.”

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We prefer to keep Eq. (18) because it is generally valid. We don't see the added value of a separate derivation of Eq. (18). It was already presented in Eq. (15) of Compernelle and Muller (2014) and can be derived in one step from Eq. (10) of Compernelle and Muller (2014), simply by evaluating  $\ln \gamma_s$  at infinite dilution and at saturation, and then taking the difference.

**Reviewer #2.** The authors need to comment on the impact of likely errors in their input data on the activity coefficient ratio. How sensitive is the activity coefficient ratio to errors in the solubility limit? How reliable are the solubility limits provided with the  $a_w$  data? Would small errors in the  $a_w$  data have a significant impact upon the calculated activity coefficient ratio?

**Author's response.**

#### **Reliability of solubility limits and impact on activity coefficient ratio**

Solubility limits were not taken from the same source as the  $a_w$  data, because it was not always clear if  $a_w$  was measured up to the solubility limit. Rather, we took the solubility limit from works where solubility was the focus (see Table 3). Based on the uncertainties that are reported, and by comparing solubility limits for the same compounds from different data sources, it can be concluded that the error on solubility measurement is generally very small. A discussion on this is included in the error analysis in the appendix. Moreover, these small uncertainties in  $x_s^{\text{sat}}$  do not affect the integration region in Eq. (18) significantly, and therefore also not the activity coefficient ratio.

#### **Impact of $a_w$ errors on activity coefficient ratio**

If the solubility limit is low, the activity coefficient ratio is necessarily close to unity and will not be affected much by errors in  $a_w$ . The situation is of course different if the solubility is large, and therefore the integration region in Eq. (18) becomes large. We applied random shifts to the  $a_w$  data, based on the precision of the data. This resulted in small uncertainties for the activity coefficient ratio. This is also included in the error

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analysis in the appendix.

**Reviewer #2.** p. 13538 line 16-17:- 'For adonitol and arabinitol ' .... the simple but successful one parameter Margules fittings of Chirife et al.' This is a bit subjective (on what basis is it successful?). Can the authors please delete 'simple but successful'.

**Author's response.** This is deleted.

**Reviewer #2.** p. 13538 line 19 '. . .but reasonable assumptions [for the activity coefficient ratio] could be made.' This demands more explanation, which you provide in Table 3, so suggest you insert '(see Table 3)' after 'made'.

**Author's response.** Reference to the table inserted.

**Reviewer #2.** p. 13539 line 1:- The first line should read "Using Eqs. (4), (5), (8) and (9). . .?"

**Author's response.** It should have been "Using Eqs. (4), (5), (8) and (10)". This is now corrected.

**Reviewer #2.** p. 13540 Eq. 20:- need a reference for the derivation of this equation.

**Author's response.** The equation has been explicitly derived instead.

**Reviewer #2.** p. 13540 line 10:- need a reference for the range of  $k^*$  in clouds. Also for the calculation of  $k^*$  for clouds and aerosol- what temperature is used?

**Author's response.** The  $k^*$  range is derived from the LWC range for cloud and aerosol given at p. 13539, and the reference temperature 298.15 K. This is now indicated in the text.

**Reviewer #2.** p. 13541 Eq. 21/22:- Need references for the derivation of these equations (or provide their derivation in an Appendix). Also the form of Eq 21 should be made clearer by putting brackets around  $f_{p,s} / (1-f_{p,s})$ .

**Author's response.** The steps needed to derive these equations from Eq. 2 have

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been mentioned and the brackets have been added.

**Reviewer #2.** p. 13542 line9-10:- What is the range of  $x_{AS}$  used and what were the corresponding RH values?

**Author's response.**  $x_{AS}$  was varied between 0.43 and 0, corresponding to an RH between 30 and 100%. This is now mentioned in the text.

**Reviewer #2.** p. 13542 line 26-28:- Sentence beginning:- 'Glycerol. . .' needs to be reworded. . . Suggest:- 'At RH=90% glycerol, with three hydroxyl groups, is 95% in the gas phase while sorbitol, with six hydroxyl groups, is still 50% in the particulate phase at RH=44%.' The authors should comment that this may be due to glycerol being much more volatile than sorbitol.

**Author's response.** We changed the sentence into:

"At RH=90% glycerol, with three hydroxyl groups, is 95% in the gas phase while sorbitol, with six hydroxyl groups, is still 50% in the particulate phase at RH=44%. This is due to the large difference (8 orders of magnitude) of their  $k_h$  values."

**Reviewer #2.** p. 13545:- Section 6.1:- in this section the authors discuss some of the uncertainties in their HLC values. However they really need to have discussed in the earlier part of the work the expected uncertainties in key inputs to HLC values such as solid state pressures and IDAC values to make this meaningful. Once they have provided some information on the sources and magnitude of likely errors for their  $p_{Cr}^0$  values and IDAC then the authors should be able to comment authoritatively on the impact on their HLC of different sources of error for different compounds. In its present form without the error estimates to back up the statements in this section are quite devoid of meaning.

**Author's response.** We have now performed a more quantitative error analysis in the appendix, deriving uncertainties for  $a_w$ ,  $\gamma_s^\infty$ ,  $p_L^0$ ,  $p_{Cr}^0$ ,  $x_s^{sat}$ ,  $\gamma_s^\infty/\gamma_s^{sat}$ ,  $\Delta H_{sub}$  or  $\Delta H_{vap}$ ,  $T_{fus}$ ,  $\Delta H_{fus}$ ,  $C_{p,Cr}$ ,  $C_{p,L}$  and  $C_{p,g}$ .

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Based on this, we are able to make a more solid discussion of the errors. We rewrote the discussion of this section:

"An error analysis is performed in Appendix A. The compounds that are liquid at room temperature (most diols and glycerol) have a relatively low uncertainty in  $k_h$  (relative standard error 6-28%). For some compounds, further improvement is possible with more precise  $p_L^0$  data and/or more fine-grained and precise  $a_w$  data in the dilute region.

The compounds that are solid at room temperature, especially the polyols with four or more hydroxy groups, bear a much larger uncertainty in  $k_h$  (relative standard error 34-82%). This is mainly due to the use of high-temperature liquid or solid state vapour pressures. More specifically, it is due to the uncertainty in  $\Delta H_{vap}$  or  $\Delta H_{sub}$  in combination with the extrapolation over a large temperature interval. For the hexols, also the uncertainty in heat capacity becomes important, although we note that the error in  $C_{p,g}$  is speculative as this property is estimated. Measuring the (solid or liquid state) vapour pressure closer to room temperature will lower these uncertainties.

As noted above, the  $C_{p,g}$  values are estimated. Improvement here is possible by using  $C_{p,g}$  derived from experiment or from ab initio calculations rather than using a group contribution method. For nonane diol and decane diol, only solubilities from a secondary reference (Merck Millipore) could be retrieved, for which it is difficult to estimate the reliability. New solubility measurements are desirable to obtain a more reliable  $k_h$  estimate."

**Reviewer #2.** Tables:- The authors should provide the chemical structures for the compounds in Tables 2 and 3.

**Author's response.** We have inserted a new table with an overview of the polyols with 3 or more hydroxyl groups, together with their molecular structure. For the diols, we did not do this, as straightforward IUPAC names are used in the text. Note that some info from Table 2 (number of OH groups, synonyms) is transferred to this new table.

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## 2.3 Technical Corrections

**Reviewer #2.** p. 13532-line15:- insert 'solute' after 'liquid' to improve clarity.

**Author's response.** 'solute' inserted.

**Reviewer #2.** p. 13533-line 2:- The sentence should read 'In the case that the solubility is small. . .'

**Author's response.** Sentence adapted.

**Reviewer #2.** p. 13536 line 2 and line 6:- The authors might consider using 'temperature correction' rather than 'transformation' to improve clarity.

**Author's response.** Sentence adapted.

**Reviewer #2.** p. 13538 line 15:- suggest 'underestimates  $\gamma_w$  of these polyol/water mixtures.'

**Author's response.** Sentence adapted.

**Reviewer #2.** p. 13541 line 12:- to improve clarity insert 'polyol' so that it reads '. . .the amount of polyol solute is infinitesimally small.'

**Author's response.** As in the subsequent lines we treat also diacids and hydroxy acids, we put instead: '... the amount of organic solute is infinitesimally small.'

## 3 Reply to reviewer 3

### 3.1 General

**Reviewer #3.** This is a good contribution for assessing the Henry's law constants of polyols some of which are of strong interest in atmospheric chemistry. Some of the de-  
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rived Henry constants are extremely high, especially for the sugar- related compounds. Here, I am missing a discussion in view of other available Henry constants and a evaluation as the final outcome of this discussion. I think some of the data listed here are not compared towards, other, existing data and I feel the manuscript should be revised accordingly. Otherwise a contribution fitting well to ACPD and thoroughly done.

**Author's response.** We thank the reviewer for this positive evaluation.

In section 6.2 a comparison with the literature was already done. We have not found any other experimental HLC data for these molecule types. Given that in the (necessarily limited) comparison with the literature the data was mostly within a factor 2 or 3, we think that the agreement is reasonable. This is now reflected more clearly in the text. We added at page 13545, line 24:

"In conclusion, for five out of six HLC values, we have a reasonable agreement with literature values."

### 3.2 Details:

**Reviewer #3.** Abstract, line 5: What does 'intermediary results' stand for here ?

**Author's response.**

We meant that in the process of deriving the Henry's law constants, also other quantities have been derived. We replaced the sentence with

"While deriving HLC and depending on the case, also infinite dilution activity coefficients (IDACs), solid state pressures or activity coefficient ratios are obtained as intermediate results."

## 4 Other changes

Unfortunately two mistakes regarding units were present in the discussion paper.

**Correction 1.** Bradley and Cotson (1953) reported their vapour pressure measurements of pentaerythritol in cm Hg, while we assumed incorrectly that it was in mm Hg. Therefore, the derived  $p_{Cr}^0(T_{ref})$  should have been  $9.2 \times 10^{-13}$  atm (or  $9.3 \times 10^{-8}$  Pa), instead of  $9.2E-14$  atm. This is now corrected in Table 2. As a consequence, we rewrote the text starting from p. 13537, line 21:

“However, due to differences in  $\Delta H_{vap}$  or  $\Delta H_{sub}$ , the extrapolated  $p_{Cr}^0(298.15\text{ K})$  is a factor 7 to 50 higher if the older data of Nitta et al. (1950, 1951); Bradley and Cotson (1953) is used, compared to when the more recent data of Barone et al. (1990) is used. In the older studies the enthalpy was determined using much less data points (6-11, compared to 25-30 for the data of Barone et al. (1990), and specifically for the data of Nitta et al. (1950, 1951), over a quite narrow temperature interval ( $\sim 12$  K, compared to 30-40 K for the other studies). Therefore, we consider the  $p_{Cr}^0$  derived from the high-temperature data of Barone et al. (1990) as more reliable.”

**Correction 2.** By mistake we inserted the solubility mass fraction of pentaerythritol (Cheon, 2005), without converting to mole fraction. This made following corrections necessary:

- $x_s^{sat}$  in Table 3 is now 0.00946 instead of 0.067.
- Due to the low solubility,  $\gamma_s^\infty/\gamma_s^{sat}$  can be approximated as 1 (Table 3). The UNIFAC-MP calculation gives now 0.97.
- $k_h$  becomes  $7.4 \times 10^{12}$  instead of  $6.7 \times 10^{13}$  (Table 4). In Figs. 2b, c, the curve belonging to pentaerythritol has moved closer to that of erythritol.

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