Atmos. Chem. Phys. Discuss., 9, 9537–9550, 2009
www.atmos-chem-phys-discuss.net/9/9537/2009/
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Atmospheric Chemistry and Physics Discussions

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Comment on Kokkola et al. (2008) – Comparisons with analytical solutions from Khvorostyanov and Curry (2007) on the critical droplet radii and supersaturations of CCN with insoluble fractions

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Received: 1 April 2009 – Accepted: 1 April 2009 – Published: 15 April 2009

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Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

Analytical solutions for the critical radii r_{cr} and supersaturations s_{cr} of the cloud condensation nuclei with insoluble fractions were derived by Khvorostyanov and Curry (2007, hereafter KC07). Similar solutions were found later by Kokkola et al. (2008, hereafter Kok08); however, Kok08 used the approximation of an ideal dilute solution, while KC07 used more accurate assumptions that account for nonideality of solutions. Kok08 found a large discrepancy with KC07 in the critical supersaturations. Various possible reasons of this are analyzed. It is shown that the major discrepancy was caused by a simple mistake in Kok08 in the equation for the critical supersaturation: erroneous "plus" sign between the Kelvin and Raoult terms instead of correct "minus" sign. If this mistake is corrected, the equations from Kok08 mostly repeat the equations from KC07, except that Kok08 use the dilute solution approximation. If the mistake in Kok08 is corrected, then the differences in the critical radii and supersaturations do not exceed 16–18%, which characterizes the possible errors of an ideal diluted solution approximation. If the Kok08 scheme is corrected and applied to a nonideal solution, then the difference with KC07 does not exceed 0.4–1%.

1 Introduction

A theoretical basis for consideration of hygroscopic growth of atmospheric aerosols or cloud condensation nuclei (CCN) and their activation into cloud drops was provided by the Köhler (1936) equation that enabled prediction of the CCN critical radii r_{cr} and supersaturations s_{cr} for drop activation. Kohler's equation was designed originally for fully soluble aerosols. However, natural aerosols are almost always mixed, i.e., contain soluble and insoluble fractions, and Köhler's equation was modified later to include insoluble fractions (for a review, see Hänel, 1976; Pruppacher and Klett, 1997, hereafter PK97; Charlson et al., 2001; Foster et al., 2007).

Simple analytical solutions for r_{cr} and s_{cr} are desirable for understanding the para-

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metric dependencies and also for developing cloud activation parameterizations for cloud and climate models. Such analytical solutions were derived by Khvorostyanov and Curry (2007, hereafter KC07) with sufficiently general assumptions and for arbitrary mass soluble fractions. It was shown in KC07 that the new equations for r_{cr} and s_{cr} transform into the classical Köhler's equations for sufficiently high soluble fraction, and yield new analytical limits for very small masses of soluble fractions where the classical equations fail. The accuracy of the new equations was verified in KC07 by comparison with experimental data, and previous particular cases.

Kokkola et al. (2008, hereafter Kok08) subsequently published a paper where similar analytical solutions were found for r_{cr} and s_{cr} for mixed CCN. However, Kok08 used an approximation of an ideal dilute solution, which often is not justified for CCN with insoluble fractions. A comparison was performed in Kok08 of the critical supersaturations for a NaCl particle that revealed a discrepancy with KC07 of up to 100%. Kok08 explained this discrepancy by an "assumption" made in KC07, but it was not clear what assumptions could cause such a great discrepancy. The possible reasons of this difference are analyzed here, including:

1. approximations in basic equations;
2. the cubic equations for the critical radii;
3. solutions of these equations;
4. other possible reasons.

Finally, it is determined that the major discrepancy between Kok08 and KC07 was caused by an elementary mistake in the equation for the critical supersaturation in Kok08: an erroneous "plus" sign between the Kelvin and Raoult terms instead of correct "minus" sign. The accuracy of an ideal dilute solution approximation used in Kok08 is estimated, it is found that the use of a non-ideal solution approximation improves the accuracy.

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2 Comparison of KC07 and Kok08

2.1 Comparison of the basic equations in both approaches

KC07 begin their derivation with the equations given in Pruppacher and Klett (1997, hereafter PK97) for water saturation ratio S_w or for supersaturation $s_w = S_w - 1$

$$s_w = \exp\left(\frac{A_k}{r} - \frac{B}{r^3 - r_d^3}\right) - 1\,, \tag{1}$$

$$A_k = \frac{2M_w\sigma_{sa}}{RT\rho_w}\,, \quad B = \frac{3\nu_s\Phi_s\varepsilon_m m_d M_w}{4\pi M_s\rho_w}\,. \tag{2}$$

Here A_k is the Kelvin curvature parameter, M_w is the molecular weight of water, σ_{sa} is the surface tension at the drop solution-air interface, R is the universal gas constant, T is the temperature (in degrees Kelvin), ρ_w is the water density, ν_s is the number of ions in solution, Φ_s is the osmotic potential, $\varepsilon_m = m_s/m_d$ is the mass soluble fraction, r_d and m_d are the radius and mass of a dry aerosol particle (CCN), m_s and M_s are the mass and molecular weight of the soluble fraction. The parameter B describes effects of the soluble fraction and KC07 parameterized it as

$$B = b r_d^{2(1+\beta)} \tag{3}$$

where the parameters b and β depend on the chemical composition and physical properties of the soluble part of an aerosol particle. For β=0.5 and β=0, the soluble fraction is proportional to the volume ($B \sim m_s \sim r_d^3$) and surface area ($B \sim m_s \sim r_d^2$), respectively. Note that KC07 do not assume that $m_s \sim r_d^3$ in the B term as in most other works, this allows to consider not only CCN with soluble fraction mixed in the volume, but also CCN with the surface soluble shells covering insoluble cores. The KC07 equations do not imply a dilute solution approximation.

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Kok08 begin their derivation using also Köhler's equation with insoluble fraction, but in another approximation

$$s_w = \exp\left(\frac{A_F}{D_p} - \frac{B_F}{D_p^3 - D_{p,0}^3}\right) - 1\,, \tag{4}$$

where $D_{p,0}$ is the equivalent diameter of the insoluble core (instead of the dry particle). The parameters A_F and B_F used by Kok08 are taken from Seinfeld and Pandis (1998, hereafter SP98), where they are specified as

$$A_F = \frac{4M_w\sigma_w}{RT\rho_w}\,, \quad B_F = \frac{6n_sM_w}{\pi\rho_w}\,, \tag{5}$$

where n_s is the number of solute moles in a drop. It is easily shown that

$$A_F = 2A_K\,, \quad B_F = 8B\,. \tag{6}$$

Note, however, that the form of the denominator in the 2nd term in Eq. (4) (D_p^3–D_{p0}^3) and of B_F in Eq. (5) used in Kok08 are given in SP98 as an approximation for ideal dilute solutions only. In the dilute approximation, the activity coefficient γ_w or osmotic coefficient Φ_s in Eq. (2) tend to unity (therefore they are absent in Eq. 5), the volume occupied by solute can be neglected relative to the droplet volume, and the volume of the wet drop is much greater than the original dry volume. These are rather severe limitations that may become invalid for CCN with small soluble fractions and solutions are not dilute even at the time of drop activation (e.g. Fig. 3 in KC07), and γ_w or Φ_s can differ from 1 even at $S_w \to 1$. More complete expressions without ideality and high dilution are given in SP98 (without coefficients A_F and B_F) and in PK97 and are accounted for in KC07 in the coefficients b in Eq. (3).

KC07's Eqs. (1) and (2) are equivalent to the nonideal approximations from SP98 or PK97 and do not assume a dilute solutions. The dilute approximation used by Kok08 can be inconsistent for CCN with high insoluble fraction, and may lead to substantial errors because the solution may be concentrated even at high humidities. This difference

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in approximations could be one of the reasons of the discrepancies between KC07 and Kok08. Kok08 state that KC07 "use approximation in the derivation of the critical radii". However, a comparison above of the basic equations from KC07 with KOK08 shows that the approximation used in KC07 is more accurate than the approximation used in KOK08.

2.2 Comparison of the cubic equations for the critical radii or diameters

The critical radius r_{cr} of a drop activation is obtained from the equation $ds(r_{cr})/dr_{cr}$ with $s_{cr}(r_{cr})$ defined by Eq. (1). This yields a sixth-order equation in r_{cr} that was reduced in KC07 to a cubic algebraic equation (Eq. (26) in KC07)

$$r_{cr}^3 + ar_{cr}^2 - r_d^3 = 0\,, \quad a = -\left(\frac{3B}{A_K}\right)^{1/2} = -\left(\frac{3br_d^{2(1+\beta)}}{A_K}\right)^{1/2}\,. \tag{7}$$

Kok08 arrived at the similar cubic equation (Eq. 4 in Kok08) identical in form to Eq. (7); the difference is in the particle size term $D_{p,0}$ instead of r_d in KC07. The term r_d in Eq. (7) is the dry radius of a CCN that includes soluble and insoluble fractions, while D_{p0} is the equivalent diameter of the insoluble fraction, which arises from using a dilute solution approximation. Thus, the differences in the results between KC07 and Kok08 are not caused by the form of the cubic equation for the critical radii, but could be partially due to the different meaning of the particle size terms.

2.3 Verification of the solution for the critical radii in KC07

The solution to Eq. (7) was found in KC07 in the form:

$$r_{cr} = r_d\chi(V)\,, \quad \chi(V) = \left[V + P_+(V) + P_-(V)\right]\,, \tag{8}$$

$$P_\pm(V) = \left(V^3 \pm \left(V^3 + \frac{1}{4}\right)^{1/2} + \frac{1}{2}\right)^{1/3}\,, \quad V = \left(\frac{br_d^{2\beta}}{3A_k}\right)^{1/2} = \frac{1}{3r_d}\left(\frac{3B}{A_k}\right)^{1/2}\,. \tag{9}$$

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The critical supersaturation s_{cr} can be calculated by substituting r_{cr} from Eqs. (8) and (9) into (1):

$$s_{cr} = \exp\left(\frac{A_k}{r_{cr}} - \frac{B}{r_{cr}^3 - r_d^3}\right) - 1 \,. \tag{10}$$

One possible reason of the discrepancy between Kok08 and KC07 could be if this solution Eq. (8) for r_{cr} does not satisfy Eq. (7). The validity of this solution can be proven if substitution of r_{cr} from Eq. (8) into Eq. (7) satisfies this equation. Denoting the left hand side of Eq. (7) as $Z r_d^3$, and substituting Eqs. (8) and (9) into Eq. (7), we obtain:

$$\begin{aligned} Z r_d^3 = &\left[r_d^3\left(V^3 + P_+^3 + P_-^3 + 3VP_+^2 + 3VP_-^2 + 3V^2P_+\right.\right. \\ &\left.\left. +3V^2P_- + 6VP_+P_- + 3P_+P_-^2 + 3P_+^2P_-\right)\right] \\ &+ \left[-3r_d^3\left(V^3 + VP_+^2 + VP_-^2 + 2V^2P_+ + 2V^2P_- + 2VP_+P_-\right)\right] + \left[r_d^3\right] \,. \end{aligned} \tag{11}$$

The square brackets denote each of the 3 terms in Eq. (7). The solution (8) is correct if we can prove that Z=0: then the left hand side is zero, and thus equal to the RHS of Eq. (7). Dividing each term in Eq. (11) by r_d^3, canceling equal terms with opposite signs and regrouping, Eq. (11) is simplified as

$$Z = -2V^3 + \left(P_+^3 + P_-^3\right) + 3(P_+ + P_-)\left(P_+P_- - V^2\right) - 1 \,. \tag{12}$$

Further simplifications can be done using the properties of the functions P_+ and P_-:

$$P_+^3 + P_-^3 = 2V^3 + 1 \,, \quad P_+P_- = V^2 = \left(\frac{1}{9r_d^2}\right)\left(\frac{3B}{A_k}\right) \,. \tag{13}$$

Substituting these relations into Eq. (12) we obtain

$$Z = -2V^3 + (2V^3 + 1) + 3(P_+ + P_-)(V^2 - V^2) - 1 \equiv 0 \,. \tag{14}$$

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The left hand side of Eq. (14) is equal to zero, and hence Eq. (7) is satisfied by the solution Eq. (8). No approximations were made in this proof; therefore, the solution is exact without additional approximation as suggested by Kok08. Thus, the solution in KC07 is correct and is not a reason for the discrepancy with Kok08.

2.4 Limiting cases with large and small insoluble fractions

Based on their numerical results, Kok08 concluded that solution in KC07 is correct only for very small soluble fraction, $\varepsilon_m \ll 1$. However, this statement is incorrect. It is seen from the definition of V in Eq. (9) that for any $\varepsilon_m \geq 0.1$, the parameter $V \gg 1$. It was shown in KC07 that the solution (10) then can be expanded by $1/V$ and has a limit for this high V as (Eq. (29) in KC07):

$$r_{\rm cr} \approx r_d \left[V + V\left(1 + \frac{V^{3/2}}{3}\right) + V\left(1 - \frac{V^{3/2}}{3}\right)\right] = \left(\frac{3B}{A_k}\right)^{1/2}, \quad (15)$$

$$s_{\rm cr} \approx \frac{2}{3r_{\rm cr}} = \left(\frac{4A_k^3}{27B}\right)^{1/2}. \quad (16)$$

where Eq. (16) follows from Eqs. (15) and (10). These are the classical Köhler's expressions; thus, the solution from KC07 gives the correct Köhler's limit for sufficiently high soluble fraction.

2.5 Comparison of analytical solutions in KC07 and Kok08

Kok08 presented analytical solution for $D_{\rm cr}$ as (notations are slightly changed here for consistency)

$$D_{\rm cr} = \frac{\alpha_2}{6} + \frac{2}{3}\left(\frac{3B_F}{A_F}\right)\frac{1}{\alpha_2} + \frac{1}{3}\left(\frac{3B_F}{A_F}\right)^{1/2}, \quad (17)$$

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where α_1 and α_2 are defined in Kok08. Simplifying the coefficients α_1 and α_2 and using Eq. (13) plus definitions of $P_\pm$ from Eq. (10), the following relations are determined:

$$\frac{\alpha_2}{6} = 2[r_d P_+(r_{p0})]\,, \quad \frac{2}{3}\left(\frac{3B_F}{A_F}\right) = 2[r_d P_-(r_{p0})]\,, \quad \frac{1}{3}\left(\frac{3B_F}{A_F}\right)^{1/2} = 2[r_d V(r_{p0})]\,, \tag{18}$$

where $V(r_{p0})$, $P_+(r_{p0})$, and $P_-(r_{p0})$ are defined by (9), but with r_{p0}=D_{p0}/2 instead of r_d. These equations express the 3 terms on the right hand side of Eq. (17) of Kok08 through the quantities used in KC07 and defined in Eq. (9) here. Substituting them into Eq. (17), we obtain

$$D_{\rm cr} = 2r_d[V(r_{p0}) + P_+(r_{p0}) + P_-(r_{p0})] = 2r_{\rm cr}(r_{p0})\,. \tag{19}$$

The last relation is based on Eq. (8) here from KC07. Thus, solutions obtained in Kok08 are identical to solutions from KC07 but are written in a slightly different form. It is not surprising, since these are both solutions to the incomplete cubic Cardano's equation (7). Thus, the form of the solutions cannot be the reason for discrepancy.

2.6 Comparison of numerical calculations

We performed calculations for the same case as in Kok08: for a particle with radius r_d=0.025 µm (D_p=50 nm), consisting of NaCl or ammonium sulfate (Kok08 considered only NaCl) with variable soluble fraction ε_m that was varied from 10^{-4} (highly insoluble CCN) to 1 (fully soluble CCN). Figure 1 shows critical radii and supersaturations calculated using the KC07 equations, here Eqs. (8), (9), and (10), compared to the classical Köhler's equations (15) and (16). One can see that the Köhler's equations have good accuracy at ε_m>0.1–0.2 for $r_{\rm cr}$ and ε_m>0.05–0.1 for $s_{\rm cr}$. At smaller ε_m, the accuracy of the classical equations decreases, and at ε_m<0.02–0.04, the classical equation leads to an unphysical result whereby $r_{\rm cr}$ becomes smaller than the original dry radius r_d=0.025 µm (horizontal line in Fig. 1a). The curves calculated with the new KC07 solutions exceed r_d and asymptotically approach it as $\varepsilon_m \to 0$. Note that $s_{\rm cr}$ predicted by the KC07 solutions tend to quite reasonable values ~4% even at very small

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ε_m, while s_{cr} obtained from the classical Kohler solution reaches 35–60% at $\varepsilon_m \rightarrow 10^{-4}$. This indicates that aerosols with very small soluble fractions can serve as effective CCN at supersaturations that could be reached in convective updrafts. The dependencies of r_{cr} and s_{cr} on the initial radius r_d and other parameters are described in KC07.

A comparison of numerical calculations with Kok08 is shown in Fig. 2. The values of r_{cr} and s_{cr} from KC07 were calculated using Eqs. (8), (9), (10). The r_{cr} and s_{cr} determined from Kok08 solutions were calculated in three ways: a) using the dilute solution approximation for A_F, B_F and Φ_s=1, but correct Eq. (10) for s_{cr}; b) using A_F, B_F without the dilute approximation, with $\Phi_s \neq 1$ and correct Eq. (10) dor s_{cr} (for ammonium sulfate only), corresponding to A_K, B in Eq. (2) as in KC07 solutions; c) using Eq. (8) from Kok08 for s_{cr}

$$s_{cr} = \exp\left(\frac{A_F}{D_{cr}} + \frac{B_F}{D_{cr}^3 - D_{p0}^3}\right) - 1 \qquad (20)$$

with an incorrect "plus" sign between the Kelvin and Raoult terms in the exponent instead of the correct "minus" sign as in Eqs. (1), (10). The relative difference between the KC07 and Kok08 solutions were calculated as $(X_{KC07} - X_{KOK08})/X_{KC07} \times 100\%$, where X denotes r_{cr} or s_{cr}.

Figure 2a and b shows that the difference between KC07 and Kok08 with corrected s_{cr} in calculations without dilute solution approximation (circles and diamonds) does not exceed 0.4–1% for both r_{cr} and s_{cr} and both NaCl and ammonium sulfate. Such a small difference is somewhat surprising because of use in solutions of different parameters: r_d including soluble and insoluble fractions in KC07 and D_{p0} including only insoluble fraction in Kok08. For small ε_m, the difference between $2r_d$ and D_{p0} is small and does not influence the solutions. For large ε_m, $2r_d$ can be substantially larger than D_{p0}, but $r_{cr} \gg r_d$, and $D_{p,cr} \gg D_{p0}$, so that the difference between $2r_d$ and D_{p0} is again unimportant. With dilute solution approximation in parameters in Kok08 but with corrected s_{cr} for ammonium sulfate (asterisks in Fig. 2a and b), the difference is greater

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but still does not exceed 16–18% for both r_{cr} and s_{cr}.

Finally, Fig. 2c shows the difference in s_{cr} between KC07 and Kok08, when s_{cr} is calculated as in Eq. (8) in Kok08 or Eq. (20) here, with erroneous sign "plus" instead of the correct "minus" between the Kelvin and Raoult terms. Now, the difference exceeds 100%. This panel (c) is similar to Fig. 1 in Kok08 and led Kok08 to conclude that KC07 method is valid only for small soluble fractions. But this conclusion is obviously wrong because it is based on calculation using an erroneous equation in Kok08.

3 Conclusions

A comparison of analytical solutions for the critical radii and supersaturations of CCN with insoluble fractions obtained by Khvorostyanov and Curry (2007) and Kokkola et al. (2008) revealed the following. The analytical solution obtained in Kok08 for the critical diameter D_{cr} has a form very similar to that in KC07 and can be rewritten in a form that exactly repeats KC07. A comparison of the analytical solutions and their numerical verification revealed very small difference between KC07 and Kok08 caused by the different choice of the dry radii and the dilute solution approximation in Kok08.

Correct evaluation of the critical supersaturations also shows very small difference between the two papers. However, the equation Eq. (8) in Kok08 for s_{cr} was written with an erroneous sign "plus" instead of correct "minus" between the Kelvin and Raoult terms, and probably was used in this incorrect form for evaluating the difference with KC07. Then the difference may exceed 100% at high soluble fraction, and this led Kok08 to a conclusion that "KC07 equations are valid only for small soluble fractions." However, this conclusion is incorrect as it was based on use of an equation with an incorrect plus sign. The solutions for r_{cr} and s_{cr} obtained in KC07 are valid over a wide range of soluble fractions, and this is confirmed by the corrected solutions to Kok08. Thus, the solutions from KC07 can be used for development of parameterization of drop activation on CCN with insoluble fractions, including the cases with very small soluble fractions.

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Acknowledgement. This research has been supported by the NASA Modeling and Parameterization Program.

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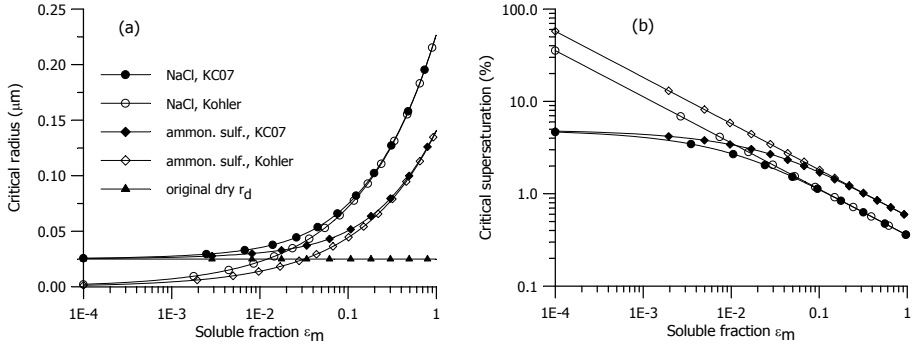

Fig. 1. Critical radii **(a)** and supersaturations **(b)** calculated as a function of the soluble fraction ε_m with analytical equations from KC07 (solid symbols) and classical Köhler's equations (open symbols) described in Sects. 2.3 and 2.4. The parameters are: particle radius r_d=0.025 μm, soluble fraction is NaCl or ammonium sulfate as indicated in the legend.

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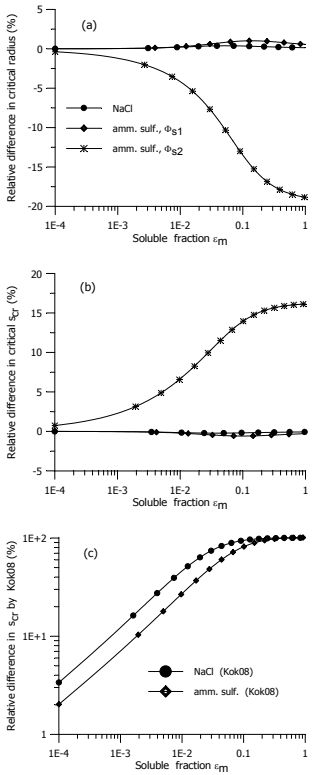

Fig. 2. The difference (%) in critical radii **(a)** and supersaturations **(b)**, **(c)** as a function of the soluble fraction ε_m calculated with analytical equations from KC07 and Kok08 as $(X_{KC07}-X_{KOK08})/X_{KC07}\times100\%$. Here X denotes r_{cr} or s_{cr}, and the subscript denotes the source work. The solid circles relate to NaCl; the diamonds relate to ammonium sulfate calculated with equations from Kok08 but corrected according KC07, i.e., without assumption on dilute solution, correct Eq. (10) for s_{cr} and $\Phi_s<1$ as in KC07. Panel **(c)** shows the difference in s_{cr} between KC07 and Kok08, exceeding 100%, when s_{cr} is calculated as in Kok08 with erroneous sign "plus" in their Eq. (8) instead of correct "minus" between the Kelvin and Raoult terms; this panel (*s*) is similar to Fig. 1 in Kok08 and led Kok08 to a conclusion that KC07 method is valid only for small soluble fractions.

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