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

V. I. Khvorostyanov[1] and J. A. Curry[2]

[1]Central Aerological Observatory, Dolgoprudny, Moscow Region, Russia
[2]School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, Georgia, USA

Abstract. Analytical solutions for the critical radii and supersaturations of the cloud condensation nuclei (CCN) with insoluble fractions were derived by Khvorostyanov and Curry (2007, hereafter KC07). These solutions generalize Köhler's solutions for an arbitrary soluble fraction of CCN, and have two limiting cases: large soluble fraction (Köhler's original solution); and a new "low soluble fraction" limit. Similar solutions were found subsequently by Kokkola et al. (2008, hereafter Kok08); however, Kok08 used the approximation of an ideal and 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. It is shown that the major discrepancy with KC07 found in Kok08 was caused by the simple mistake in Kok08, where comparison was made not with the general solution from KC07, but with the Köhler's solution or with some unknown quantity, not even with the "low soluble fraction" limit. If general solutions from the two works are compared, the equations from Kok08 mostly repeat the equations from KC07, except that Kok08 use the ideal 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 errors of the ideal dilute solution approximation. If the Kok08 scheme is modified following KC07 to account for the non-ideality of 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 (e.g., Hänel, 1976; Pruppacher and Klett, 1997, hereafter PK97; Charlson et al., 2001; Ghan et al., 1993, 1995; Kulmala et al., 1993; Levin et al., 1996; Shulman et al., 1996; Laaksonen et al., 1998; Seinfeld and Pandis, 1998; Lohmann, and Feichter, 2005; McFiggans et al., 2006; Khvorostyanov and Curry, 2006, 2008; Foster et al., 2007).

Simple analytical solutions for r_{cr} and s_{cr} are desirable for understanding the parametric 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 a new analytical "low soluble fraction limit" 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

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for r_{cr} and s_{cr} for mixed CCN. However, Kok08 used the approximations of an ideal and dilute solution, which often is not justified for CCN with insoluble fractions (e.g., PK97; Lohmann, and Feichter, 2005; McFiggans et al., 2006; Foster et al., 2007). A comparison of the critical supersaturations for a NaCl particle was performed in Kok08 that revealed a discrepancy with KC07 of up to 100%, especially for large soluble fraction. Kok08 explained this discrepancy by an "assumption" made in KC07, but it was not clear what assumptions could cause such a great discrepancy. The comparisons with Kok08 are made and possible reasons for this difference are analyzed here, including: 1) approximations in basic equations; 2) the cubic equations for the critical radii; 3) analytical solutions of these equations; 4) numerical solutions. Finally, it is determined that the major discrepancy between Kok08 and KC07 was caused by an elementary mistake in Kok08, whereby the Köhler's or some unknown quantity (not even the "low soluble fraction limit") were used in Kok08 for comparison instead of the general solution from KC07. The accuracy of an ideal dilute solution approximation used in Kok08 is estimated, and it is found that the use of a non-ideal solution approximation as in KC07 improves the accuracy.

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 PK97 for water saturation ratio S_w or for supersaturation $s_w = S_w - 1$

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

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

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 is the drop radius, 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

$$B = br_d^{2(1+\beta)} \qquad (3)$$

where the parameters b and β depend on the chemical composition and physical properties of the soluble part of an aerosol particle. For $\beta = 0.5$ and $\beta = 0$, 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 consideration not only of CCN with soluble fraction mixed in the volume, but also CCN with surface soluble shells covering insoluble cores (e.g., Levin et al., 2006). The KC07 equations do not imply a dilute or ideal solution approximation.

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

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

where D_p is the drop diameter, $D_{p,0}$ 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

$$A_F = \frac{4M_w\sigma_w}{RT\rho_w}, \quad B_F = \frac{6n_s M_w}{\pi\rho_w}, \qquad (5)$$

where n_s is the number of solute moles in a drop. It is easily shown that when the dilute solution approximation is applied to B, then

$$A_F = 2A_K, \quad B_F = 8B. \qquad (6)$$

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 limitations may become invalid for CCN with small soluble fractions and solutions are not dilute particularly at the time of drop activation, and γ_w or Φ_s can differ from 1 even at $S_w \to 1$ (e.g., Hänel, 1976; PK97, Table 6.3). In particular, this is illustrated by Fig. 3 in KC07, where the ratio r_{cr}/r_d is close to 1 for small r_d and ε_m, i.e., the solution is concentrated and nonideal. More complete expressions without assuming 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 (3).

KC07's Eqs. (1) and (2) are equivalent to the nonideal approximations from SP98 and PK97 and do not assume a dilute solution. 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 in approximations is one of the reasons for 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 condition of maximum, $ds(r_{cr})/dr_{cr} = 0$, with $s_{cr}(r_{cr})$ defined by (1). This yields a sixth-order equation in r_{cr} that was reduced in KC07 to a cubic algebraic equation [Eq. (26) in KC07]

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

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 difference in the results between KC07 and Kok08 is 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:

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

$$P_\pm(V) = \left(V^3 \pm \left(V^3 + \frac{1}{4}\right)^{1/2} + \frac{1}{2}\right)^{1/3}, \tag{9}$$

$$V = \left(\frac{b r_d^{2\beta}}{3 A_k}\right)^{1/2} = \frac{1}{3 r_d}\left(\frac{3B}{A_k}\right)^{1/2}.$$

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 for 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 (7) satisfies this equation. Denoting the left hand side of Eq. (7) as $Z r_d^3$, and substituting Eqs. (8) and (9) into (7), we obtain:

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

Each square bracket denotes 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 (7). Dividing each term in (11) by r_d^3, canceling equal terms with opposite signs and regrouping, then (11) is simplified as

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

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

$$P_+^3 + P_-^3 = 2V^3 + 1, \tag{13}$$

$$P_+ P_- = V^2 = \left(\frac{1}{9 r_d^2}\right)\left(\frac{3B}{A_k}\right). \tag{14}$$

Substituting these relations into Eq. (12), we obtain

$$Z = -2V^3 + (2V^3 + 1) + 3(P_+ + P_-)(V^2 - V^2) - 1 \equiv 0. \tag{15}$$

The left hand side of Eq. (15) is equal to zero, and hence Eq. (7) is satisfied by the solution (8). No approximations were made in this proof; therefore, the KC07 solution is exact and 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 the 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 (8) then can be expanded by $1/V$ and has a limit for this high V as (Eq. 29 in KC07):

$$r_{cr} \approx \tag{16}$$
$$r_d\left[V + V\left(1 + \frac{V^{3/2}}{3}\right) + V\left(1 - \frac{V^{3/2}}{3}\right)\right] = \left(\frac{3B}{A_k}\right)^{1/2},$$

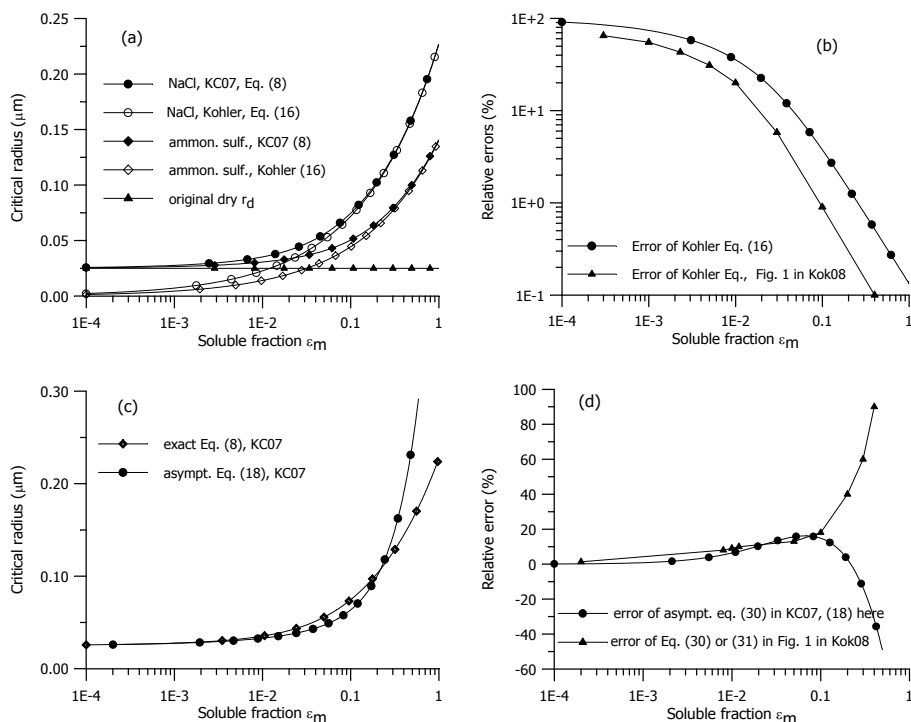$$s_{cr} \approx \frac{2}{3 r_{cr}} = \left(\frac{4 A_k^3}{27B}\right)^{1/2}. \tag{17}$$

Fig. 1. Critical radii in μm (a, c) calculated with exact Eq. (8) here [(27) in KC07], and approximations (16, Kohler) and (18, "low-soluble fraction") and the relative errors in % (b, d) of Kohler Eq. (16) here [Eq. (29) in KC07] at $V \gg 1$, and asymptotic Eq. (18) [Eq. (30) in KC07] at $V \ll 1$. Relative errors in (b, d) were calculated using Eqs. (8), (16), and (18) here and compared to the corresponding "dashed" and "solid" curves in Fig. 1 in Kok08.

Here, (17) follows from (16) and (10), that are the classical Köhler's expressions. Thus, the solution from KC07 gives the correct Köhler's limit for sufficiently high soluble fraction. In the opposite limit at very small soluble fractions or radii, when $V \ll 1$, another expansion of (8) by V was applied and a new "low solubility" limit was obtained in KC07:

$$r_{cr} \approx \tag{18}$$

$$r_d(1 + V + \frac{2}{3}V^3) = r_d \left[1 + \left(\frac{br_d^{2\beta}}{3A_k} \right)^{1/2} + \frac{2}{3} \left(\frac{br_d^{2\beta}}{3A_k} \right)^{3/2} \right].$$

The critical supersaturation is then calculated from the equation

$$s_{cr} = \exp\left(\frac{A}{r_{cr}} - \frac{br_d^{2(1+\beta)}}{r_{cr}^3 - r_d^3} \right) - 1 = \exp\left(\frac{2A}{3r_{cr}} \right) - 1. \tag{19}$$

2.5 Comparison of analytical solutions in KC07 and Kok08

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

$$D_{cr} = \frac{\alpha_2}{6} + \frac{2}{3}\left(\frac{3B_F}{A_F} \right)\frac{1}{\alpha_2} + \frac{1}{3}\left(\frac{3B_F}{A_F} \right)^{1/2}, \tag{20}$$

with α_1 and α_2 defined in Kok08 as

$$\alpha_2 = \left[108D_{p0}^3 + 8\left(\frac{3B_F}{A_F} \right)^{3/2} + \alpha_1 \right]^{1/3}, \tag{21}$$

$$\alpha_1 = 12\left[81D_{p0}^6 + 12D_{p0}^3 \left(\frac{3B_F}{A_F} \right)^{3/2} \right]^{1/2}$$

Simplifying the coefficients α_1 and α_2 and using Eq. (13) plus definitions of $P_{\pm}$ and V from Eq. (9), the following relations are determined:

$$\frac{\alpha_2}{6} = 2[r_d P_+(r_{p0})], \tag{22}$$

$$\frac{2}{3}\left(\frac{3B_F}{A_F} \right)\frac{1}{\alpha_2} = 2[r_d P_-(r_{p0})],$$

$$\frac{1}{3}\left(\frac{3B_F}{A_F} \right)^{1/2} = 2[r_d V(r_{p0})],$$

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 Kok08's Eq. (20) through the quantities used in KC07 and defined in (9) here. Substituting them into (20), we obtain

$$D_{cr} = \quad\quad\quad\quad\quad\quad\quad\quad (23)$$
$$2r_d[V(r_{p0}) + P_+(r_{p0}) + P_-(r_{p0})] = 2r_{cr}(r_{p0}).$$

The relation in (23) is based on Eq. (8) here from KC07. Thus, solutions obtained in Kok08 are identical to solutions from KC07 but with replacement $r_d \rightarrow r_{p0}$ and 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 $r_d = 0.025\ \mu$m ($D_p = 50$ 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 calculated using the general Eqs. (8) and (9) here (Eqs. 27, 28 in KC07), compared to the limit $r_{cr,\text{high}}$ for high soluble fraction ε_m, which is the classical Köhler's Eq. (16) (Eq. 29 in KC07), and to the limit $r_{cr,\text{low}}$ for low ε_m, in (18) (Eq. 30 in KC07).

Figure 1a shows that the Kohler's equation for r_{cr} has good accuracy at $\varepsilon_m > 0.1$–0.2. At smaller ε_m, the accuracy of the classical equations decreases, and at $\varepsilon_m < 0.02$–0.04, the classical equation leads to an unphysical result whereby r_{cr} becomes smaller than the original dry radius $r_d = 0.025\ \mu$m (horizontal line in Fig. 1a). The curves calculated with the new KC07 solutions exceed r_d and asymptotically approach it as $\varepsilon_m \rightarrow 0$. Figure 1a shows that r_{cr} is quite comparable with r_d at $\varepsilon_m \leq 0.01$–0.03, i.e., the mass of the critical wet CCN is comparable to the mass of the dry CCN, and solution is not dilute and ideal at the time of activation, in contrast to the assumption in Kok08.

The curve $r_{cr,\text{low}}$ for "low-soluble fraction limit", Eq. (18) here, is shown in Fig. 1c. It is close to r_{cr} up to $\varepsilon_m < 0.1$, and the limit $r_{cr,\text{low}}$ substantially exceeds the exact value r_{cr} at larger ε_m. The error of the Kohler's equations was analyzed in detail in KC07. It is also illustrated in Fig. 1b here and shows that the error of Köhler's equation exceeds 5% at $\varepsilon_m < 0.1$ and exceeds 50% at $\varepsilon_m < 0.01$. Figure 1d shows that the error of the "low-ε_m limit" (18) grows from zero at very small ε_m to about 20% at $\varepsilon_m \sim 0.1$, and exceeds 50% at $\varepsilon_m > 0.3$.

Kok08 illustrated the "errors" of KC07 equations for supersaturation with the "dashed" and "solid" lines in their Fig. 1. In the Interactive Discussion (Kokkola, 2009, Kok09) of the ACPD version of this paper, Dr. Kokkola admitted that the calculations in Kok08 were erroneous, and this led in Kok08 to the wrong conclusions on the validity of KC07 equations. However, no new quantitative explanations or comparisons were given in Kok09 and the meaning of the "dashed" and "solid" lines in Fig. 1 in Kok08 remained unclear. Kok08's "dashed line" is reproduced in Fig. 1b (trian-
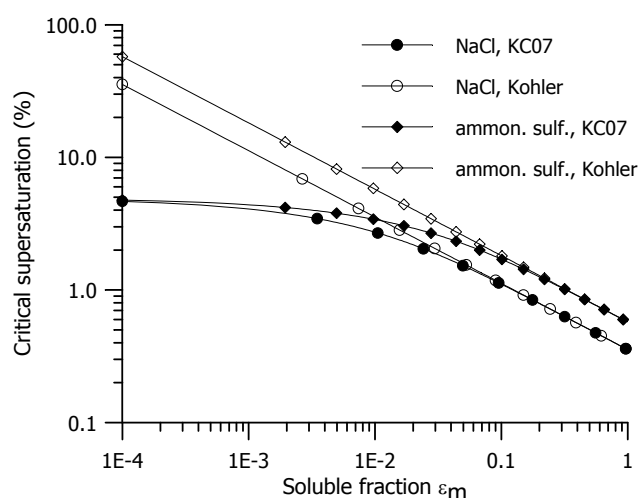

Fig. 2. Critical supersaturations calculated as a function of the soluble fraction ε_m with analytical equations from KC07 (solid symbols) and in the approximation with the old Köhler's Eq. (17) here or (24) in KC07. The parameters are: particle radius $r_d = 0.025\ \mu$m, soluble fraction is NaCl or ammonium sulfate as indicated in the legend.

gles), and compared with calculations here, both lines show a good correlation. However, this "dashed line" in Kok08 has another meaning than was interpreted in Kok08: a) it is the error in the critical radius but not in critical supersaturation as was stated in Kok08; b) it is the error not of KC07 equation, but the error of the Köhler approximation relative to more general equation for r_{cr} from KC07, and this error was already calculated in KC07. Therefore, a "comparison with KC07" with the dashed line in Kok08 was misleading, and Kok08's analysis could not draw any valid conclusions on the accuracy of the new KC07 equations comparing with the old Köhler equation.

The "solid line" from Fig. 1 in Kok08 is compared in Fig. 1d with the calculated error of the "low-ε_m approximation" (Eq. 18 here or (30) in KC07). At soluble fraction $\varepsilon_m \leq 0.1$, both curves are sufficiently close, but the curves diverge at $\varepsilon_m > 0.1$: Kok08 goes steeply upward, and the curve of correct error goes down to negative values. Thus, the solid line from Kok08 described something different but not the error of the "low-ε_m approximation"; hence it was also irrelevant for evaluation of KC07 and could not be a basis for any conclusions on its validity.

Figure 2 shows the critical supersaturations calculated with Eqs. (8)–(10) for NaCl and ammonium sulfate. They increase with decreasing soluble fraction, however, KC07 equations predict much slower increase than the Köhler's equation, which has good accuracy at $\varepsilon_m > 0.05$–0.1 for s_{cr} but fails at smaller ε_m. The s_{cr} predicted by the KC07 solutions tend to quite reasonable values $\sim 4\%$ even at very small ε_m, while s_{cr} obtained from the classical Kohler solution reaches 35–60% at $\varepsilon_m \rightarrow 10^{-4}$. This indicates that aerosols
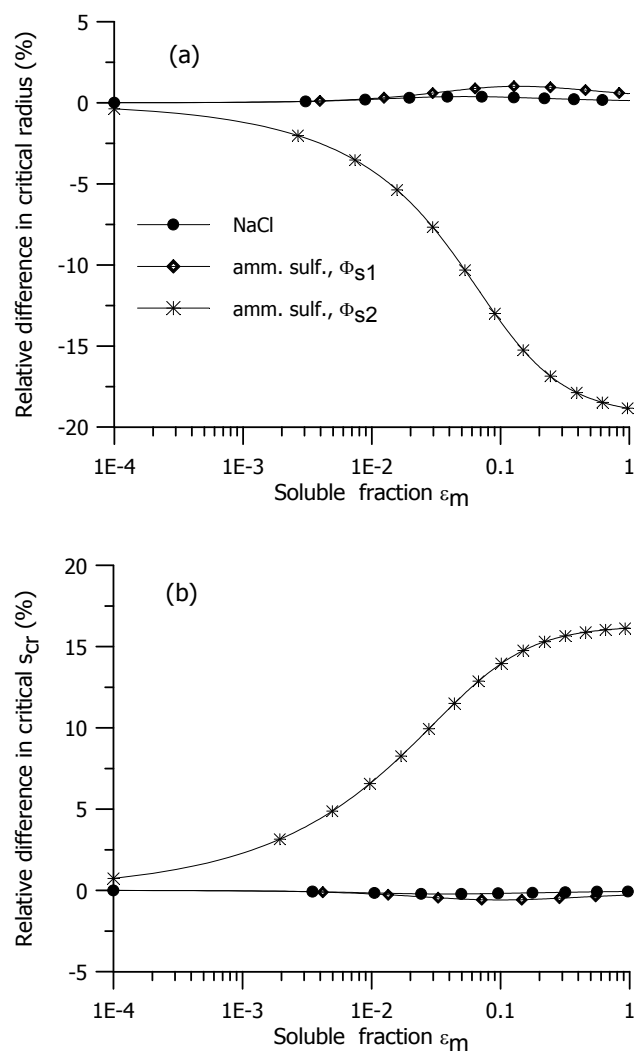
Fig. 3. The difference (%) in critical radii (a) and supersaturations (b) as a function of the soluble fraction ε_m calculated with analytical equations from KC07 and Kok08 as $(X_{KC07} - X_{Kok08})/X_{KC07} \times 100\%$. Here X denotes r_{cr} or s_{cr}, and the subscript denotes the source work. Parameters are the same as in Fig. 1 and in Kokkola et al. (2008). The solid circles relate to NaCl. The asterisks relate to ammonium sulfate calculated with dilute and ideal solution approximation as in Kok08, with $\Phi_{s2} = 1$, then the difference reaches 16–18%. The diamonds relate to ammonium sulfate calculated with equations from Kok08 but corrected according to KC07, i.e., without assumption on dilute solution and $\Phi_{s1} < 1$ as in KC07, then the difference between both methods does not exceed 0.4–1%.

with very small soluble fractions (e.g., mineral dust covered by a thin soluble film as observed by Levin et al., 1996) 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 correct comparison of calculations of KC07 with Kok08 is shown in Fig. 3. The values of r_{cr} and s_{cr} from KC07 were calculated using Eqs. (8)–(10). The r_{cr} and s_{cr} determined from Kok08 solutions were calculated in two ways: a) using the dilute and ideal solution approximation for A_F, B_F in (5) and $\Phi_s = 1$ as adopted in Kok08; b) with correction of Kok08 based on KC07, i.e., generalizing A_F, B_F without the dilute approximation and with $\Phi_s \neq 1$ (for ammonium sulfate only), corresponding to A_K, B in (2) as in KC07 solutions. 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 3a, b shows that with Kok08 equations as they are, i.e., with dilute and ideal solution approximation in parameters in Kok08 for ammonium sulfate, the difference between KC07 and Kok08 does not exceed 16–18% for both r_{cr} and s_{cr} (asterisks in Fig. 3a, b). Thus, a correct comparison shows that equations from Kok08 yield results close to KC07, and the 16–18% discrepancy is associated with the use in Kok08 of the approximation of dilute and ideal solution. Note the error associated with the ideal solution approximation can be much greater for the substances with lower osmotic potentials or activity coefficients. If Kok08 equations are corrected following KC07, i.e., without approximations of dilute and ideal solution, the difference does not exceed 0.4–1% for both r_{cr} and s_{cr} and both NaCl and ammonium sulfate (circles and diamonds).

3   Conclusions

The analytical solutions for the critical radii r_{cr} and supersaturations s_{cr} for CCN activation derived in Khvorostyanov and Curry (2007) for the arbitrary CCN soluble fraction ε_m are correct. This was proven here by direct substitution of the solution into the original equation and analysis of the original cubic equation for r_{cr}. These solutions convert into the classical Köhler's equations for the sufficiently high soluble fraction ≥ 0.1–0.2, generalize them for arbitrary soluble fraction, and tend to the other new (non-Köhler's) limit for very small ε_m. This was proven by deriving the analytical limits from the general solution.

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, can be rewritten in a form that exactly repeats KC07, and represent a particular case of solutions from KC07 but with the additional approximations of an ideal and dilute solution adopted in Kok08.

A comparison of the corresponding numerical solutions revealed that the difference between KC07 and Kok08 is much smaller than 100% found in Kok08, and is caused mostly by the approximations made in Kok08. If equations

from Kok08 are used as they are, i.e., in approximation of an ideal and dilute solution, then the difference between KC07 and Kok08 does not exceed 16–18%. If equations from Kok08 are corrected following KC07, i.e., without assumption of solution ideality and high dilution, the difference does not exceed 0.4–1%.

A conclusion made in Kok08 – that equations from KC07 are valid only for the low soluble fraction and that the difference between KC07 and Kok08 may exceed 100% – was incorrect and based on erroneous calculations of the difference between the two works in Kok08. For some unclear reason, Kok08 compared their solutions not with the general solution from KC07, but with the Köhler's solution (dashed line in Fig. 1 in Kok08) or some unknown quantity (solid line in Fig. 1 in Kok08), which does not match any of the quantities from KC07, not even the "low soluble fraction" limit.

An analysis of the possible reasons of this difference between KC07 and Kok08 was additionally complicated by the misprint in the final equation for supersaturation in Kok08: the Eq. (8) for s_{cr} in Kok08 was written with an erroneous sign "plus" instead of correct "minus" between the Kelvin and Raoult terms. The analytical and numerical study performed in this work, along with the interactive discussion at ACPD web site, allowed to establish the validity of the KC07 work, clarify the misprints and errors in Kok08, and to find the relation between the two works. Thus, the solutions for r_{cr} and s_{cr} obtained in KC07 are valid over a wide range of soluble fractions, and can be used for development of parameterization of drop activation on mixed CCN, including the cases with very small soluble fractions. In particular, the two versions of such parameterizations were developed in KC07 and Khvorostyanov and Curry (2008).

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