

**Reply to Interactive comment by Dr. Kokkola (2009)
on comment by Khvorostyanov and Curry (2009)**

We did not find any new arguments in the reply by Dr. Kokkola (2009, hereafter, Kok09) that can reject the major conclusions made in the Comment in ACPD by Khvorostyanov and Curry (2009, hereafter KC09) on the Note by Kokkola et al. (2008, hereafter Kok08) with comparison with Khvorostyanov and Curry (2007, hereafter KC07).

The only new addition in Kok09 was that a mistake in Eq. (8) for supersaturation in Kok08 was only typo but not a real mistake. If so, then the reason for the large discrepancy between KC07 and Kok08 shown in Fig. 1 in Kok08 becomes even more unclear. Kok09 did not clarify comparisons with KC07 in Kok08 but added a new confusion because some comments in Kok09 are in conflict with Kok08.

The caption to Fig. 1 in Kok08 was: “Relative error in the critical supersaturation using approximations made by Khvorostyanov and Curry (2007) compared to the analytical solutions given here in Eq. (8). **The solid curve is the relative error of Eq. (31) and the dashed curve is the relative error of Eq. (29) by Khvorostyanov and Curry (2007).**” Thus, Kok08 compared with 2 equations from KC07, (29) and (31). These comparisons are analyzed below.

1) Eq. (29). It was shown in KC07 that the newly derived general equation for r_{cr} convert into the Köhler’s equation in a limiting case with soluble fraction greater than ~ 0.1 - 0.2 . This classical Köhler’s equation (limit) is the Eq. (29) in KC07, and there was a detailed comparison in KC07 of its accuracy compared to more general equations derived in KC07, for various radii and soluble fractions. This is illustrated in Fig. 1 here. The “dashed line” from Kok08 repeat this comparison, but only for soluble fraction. This Kok08’s “dashed line” is reproduced here in Fig. 1b (triangles), and compared with similar calculations in KC07, both lines show a good correlation. However, this “dashed line” in Kok08 is twice irrelevant for a comparison with KC07: a) it is in conflict with the cited caption from Kok08, it is the error in the critical error in critical radius but not in critical supersaturation; b) it is the error not of KC07 but of the Köhler

approximation, and this error was calculated in KC07. Therefore, Kok08 could not draw any conclusions on the accuracy of new KC07 equations comparing with the old Köhler equation. Thus, a “comparison with KC07” with the dashed line in Kok08 is completely irrelevant and misleading.

2) Eq. (31) or (30). The solid line in Fig. 1 in Kok08 is even more confusing. As the cited caption from Kok08 says: “The solid line is the relative error of Eq. (31) from KC07”. This solid line goes higher than 100 in fractional units, or higher than 10,000 %, this line in % is reproduced in Fig. 1d here, triangles. However, this calculation was certainly wrong in Kok08. As it was shown in our comment in ACPD (KC09), the correctly calculated discrepancy between KC07 and Kok08 does not exceed 18-20 % with dilute solution approximation in Kok98, and does not exceed 0.4-1 % if Kok08 is corrected following KC07, i.e., without dilute solution approximation.

Thus, it is completely unclear what was shown as solid line in Fig. 1 in Kok08. After we noted this in ACPD, Dr. Kokkola changed his opinion about what he has compared in Kok08 and Kok09 suggests now that the results were compared not with Eq. (31) but “with Eq. (30) from KC07 which is the approximation for the small soluble fractions”. This is again twice unclear: a) This is in conflict with Kok08 saying that comparison was with Eq. (31); b) Eq. (30) in KC07 is not the equation for supersaturation but a limiting case for critical radius for small ε_m ; if really comparison in Kok08 was made with (30) in KC07, then no conclusions at all could be made about accuracy of critical supersaturation, because not a single comparison with s_{cr} from KC07 was done in Kok08.

However, even this statement in reply Kok09 is wrong. We checked it now and performed a new comparison with Eq. (30). Fig. 1d here shows the correctly calculated error of approximate Eq. (30) relative to Eq. (27) in KC07 (solid circles), compared to the “solid curve” in Fig. 1 in Kok08 (triangles here). 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 correct error goes down to negative values. Thus, the statement in reply Kok09 is again wrong, and comparison could not be made with Eq. (30) in KC07, and it remains a mystery what with what Kok08 and Kok09 compared. But it is clear that any correct reliable comparisons like those in KC09 and here were absent in Kok08 and a conclusions in Kok08 on the limits of validity of KC07 were artificially constructed of nothing and were wrong.

Vice versa, the accuracy of the equations derived in Kok08 is worse than in KC07. Unfortunately, our remark on possible errors of dilute solution approximation was unheard by Dr. Kokkola. Eq. (1) in reply Kok09 can be valid only for the dilute solutions. Kok09 refers to Seinfeld and Pandis (1998). This book gives an equation for S_w like Eq. (1) in Kok09 on page 792, eq. (15.38). However, SP98 emphasized that it is valid *only for dilute solutions*. Note also that it is valid only for ideal solutions since the activity coefficient is 1 in this equation. A more complete equation (15.37) is given in Seinfeld and Pandis (1998) just a few lines earlier, on page 791, it is valid for non-diluted and non-ideal solutions, but is not written with coefficients A and B as analytical solution Kok08 require. It was shown in KC09 (Fig. 2) that the use of dilute and ideal solution approximation in Kok08 may cause an additional error of several tens percent; this approximation in Kok08 and an additional error are not justified because an analytical solution can be obtained for non-dilute and anon-ideal solutions as it was done in KC07.

Conclusions

The reply by Dr. Kokkola (2009) did not provide any new information that can discard the conclusions in KC09 and does not change the major conclusions of KC09 that remain the same. Calculations shown in Fig.1 in Kok08 were irrelevant or incorrect, not a single comparison with critical supersaturations from KC07 was made; therefore a comparison with KC07 was erroneous. The conclusion in Kok08 that KC07 is valid only for very small soluble fraction was based on nothing and is incorrect. The dilute and ideal solution approximation used in Kok08

may lead to substantial errors exceeding 10% for some substances and CCN radii; this error can be substantially greater for some radii and substances where non-ideality is essential. Therefore, the equations derived in Kok08 mostly repeat solutions obtained in KC07 but make more assumptions than KC07, and hence are less accurate than KC07 over the broad range of conditions.

References

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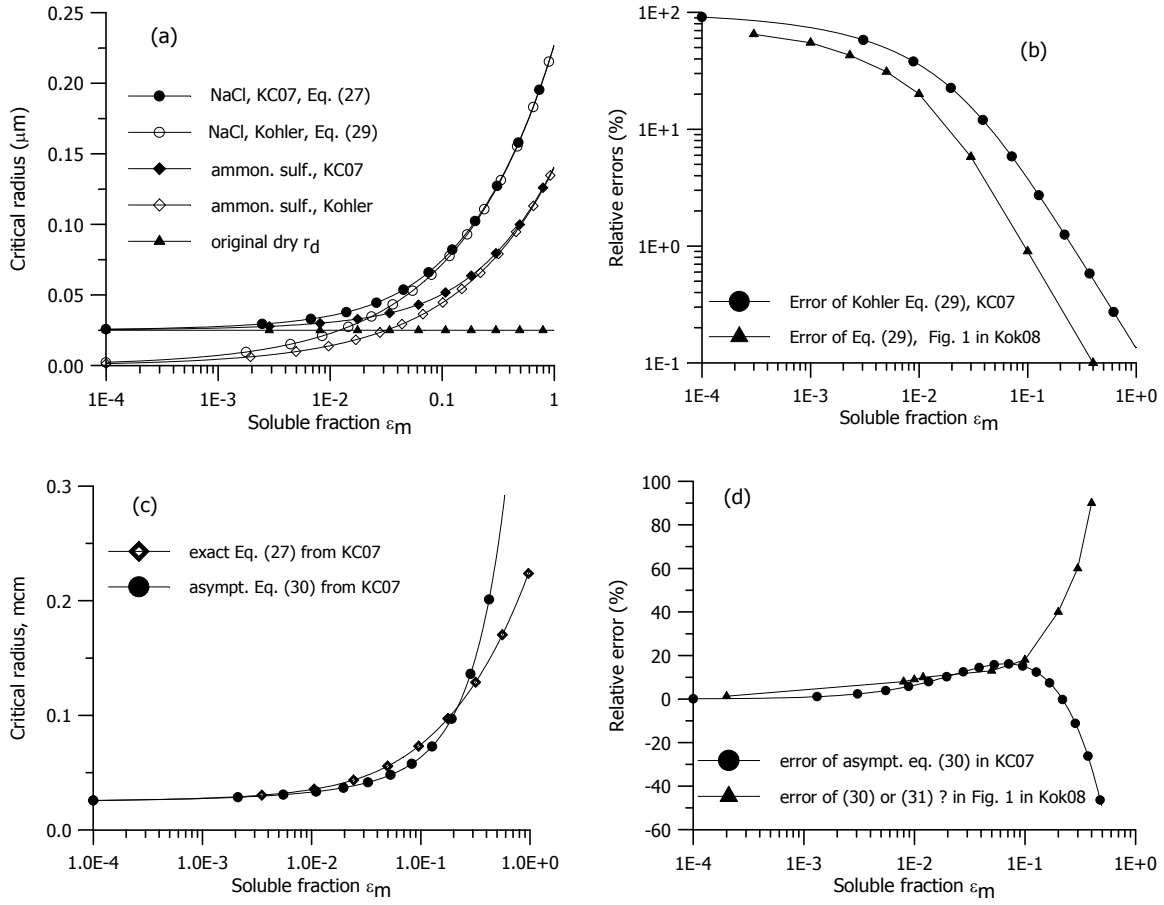


Fig. 1. Critical radii in μm (a, c) and relative errors in % (b, d) of Kohler Eq. (29), $V \gg 1$, and asymptotic Eq. (30), $V \ll 1$. Relative errors in 1b, d calculated using Eqs. (27), (29), and (30) from KC07 and compared to the corresponding curves in Fig. 1 in Kok08.