

1 APPLICATION OF KOHLER THEORY: MODELING CLOUD CONDENSATION 2 NUCLEI ACTIVITY

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7 Introduction

8 Small solid or liquid particles suspended in air known as aerosols have adverse impacts
9 on global climate through direct interactions with incoming solar radiation, as well as their
10 ability to form clouds via water uptake processes. It is established that cloud condensation
11 nucleus (CCN) activity is a complex function of aerosol size, shape, and chemical composition¹,
12 and is an important metric for investigating aerosol impacts on climate and the environment².
13 While empirical CCN measurements on ambient aerosol have been recently conducted³⁻⁷, the
14 extent to which size and/or composition drives the CCN activity of a given aerosol is still
15 unclear. The current study utilizes classical Köhler Theory to interrogate effects of mass,
16 solubility, and composition on the CCN activity of atmospheric aerosols.

17 Köhler Theory is a comprehensive approach to modeling CCN activity by incorporating
18 various physicochemical properties of aerosols, such as surface tension, density, and ionic
19 contributions of soluble components⁸.

$$20 \frac{e(r, n_{solt})}{e_s} = \left(1 - \frac{b}{r^3}\right) \exp(a/r) \quad \text{Equation 1}$$

21 Here, coefficients must be defined to incorporate size-dependent changes in surface
22 curvature and tension, as well as compositionally-dependent contributions of soluble ionic
23 components. The size dependence of surface curvature can be modeled *via* the Kelvin Effect,
24 with a coefficient defined as follows:

$$25 a = \frac{\sigma_{lv}}{\rho_l R_v T} \quad \text{Equation 2}$$

26 where σ_{lv} is the surface tension of water at a liquid-air interface, ρ_l is the density of liquid water,
27 R_v is the gas constant for moist air, and T is temperature. Dissolved ionic species will decrease
28 the equilibrium vapor pressure for water *via* the Raoult effect, with a coefficient defined as
29 follows:

$$30 b = \frac{3iM_v n_s}{4\pi\rho_l} \quad \text{Equation 3}$$

31 where i is the van't Hoff factor, M_v is the molar mass of water, n_s is the moles of solute and ρ_l is
32 the density of liquid water.

33 While this theory is well-suited for soluble species of a given size, atmospheric aerosol
34 commonly exist as compounds with both soluble and insoluble components. Because these
35 mixed-component aerosols can still act as cloud condensation nuclei, extending Köhler Theory
36 to model them is of interest.

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40 **Model Description**

41 To modify the Köhler equation in order to account for insoluble materials, we considered
42 the case of a wet particle with a soluble component and an insoluble component. The following
43 assumptions were made: (1) the soluble compound is perfectly soluble, disassociates completely
44 and does not contribute the total volume of the particle significantly; (2) the insoluble compound
45 is perfectly insoluble; (3) no internal mixing of the soluble and insoluble components; (4) the wet
46 particle is a sphere; (5) the surface tension does not change with added solute and hence the
47 Kelvin effect does not need to be modified; (6) the temperature is constant at 273 K (0°C); and
48 (7) thermodynamic processes are ignored.

49 Our model used a modified Köhler equation (see supplemental information for the
50 derivation) to calculate the water saturation over a range of wet radii:

$$51 \quad \frac{e_s(r, n_{solt})}{e_s} = \left(1 - \frac{b}{r^3 - r_i^3}\right) \exp(a/r) \quad \text{Equation 10}$$

52 The local maximum of the saturation curve determined the values of the critical
53 supersaturation and critical radius. In order to validate the accuracy of our model, we used the
54 assumptions described previously to replicate Table 5.1⁸ and maintained these assumptions
55 throughout.

56 Three sensitivity tests were conducted which represent atmospherically relevant scenarios
57 mixed-component aerosols may undergo during their lifetimes. The first test examined the
58 explicit role of particle mass on the critical radius for CCN activation by maintaining a constant
59 soluble mass fraction, χ_s , and varying the total mass, m_{tot} , which equals the sum of masses of the
60 soluble and insoluble components. Throughout the model the insoluble component was hexane,
61 for consistency. This modification changed the value of the variables b and r_i to include the
62 respective solute mass and volume of insoluble component. This sensitivity test mimicked the
63 aggregation of small aerosols of same composition to form larger aerosols. Although it is
64 unlikely for aerosols of totally identical composition to aggregate without the addition of a
65 dissimilar component, this result shows the general dependence of particle size to saturation
66 ratio.

67 The second sensitivity test investigated the effect of soluble mass fraction on critical
68 supersaturation. Total mass was held constant, mimicking the aging of an aerosol as the fraction
69 of insoluble component increases over time without contributing to the total particle mass. Fixing
70 total mass equal to 10^{-19} kg, the mass fractions 0.1, 0.5, and 1.0 were investigated which changed
71 the value of both b and r_i in our modified Köhler equation. From these results we determined the
72 approximate dependence of water uptake on mixed-component particles.

73 The final test investigated the chemical compositional changes a particle has on the
74 activation behavior. A totally soluble ($\chi_s = 1$) and mixed-component ($\chi_s = 0.5$) particle were
75 compared, each with two different van't Hoff factors which isolates the dependence of ionic
76 behavior on CCN activation based on Köhler Theory approximations. The van't Hoff factor
77 accounts for the number of dissociated ions contributing to water uptake which is
78 compositionally dependent, therefore the molecular weight value also changed for the particular

79 soluble compound. Therefore, this test essentially modeled the saturation dependence on the ratio
80 of i/M_s for solutes which have been found in atmospheric aerosols.

81 These modifications to Köhler Theory allow for a more complex modeling system.
82 However, it does not consider components that have limited or partial solubility in water. It also
83 neglects the effect of dissolved solute on the surface tension of the droplet. These omissions
84 could serve to over or underestimate a particle's critical radius and critical supersaturation,
85 depending upon its composition.

86

87 **Results and Discussion**

88 The results of the first sensitivity test (Figure 1) show that increasing total particle
89 diameter while keeping the mass fraction and identity of solute constant leads to a decrease in
90 critical supersaturation. Essentially, larger particles are easier to activate.

91 The results of the second sensitivity test (Figure 2) show that for a constant mass a
92 greater fraction of solute in the particle decreases the value of critical supersaturation. Based on
93 this result, particles with a greater mass fraction of insoluble component are harder to activate.

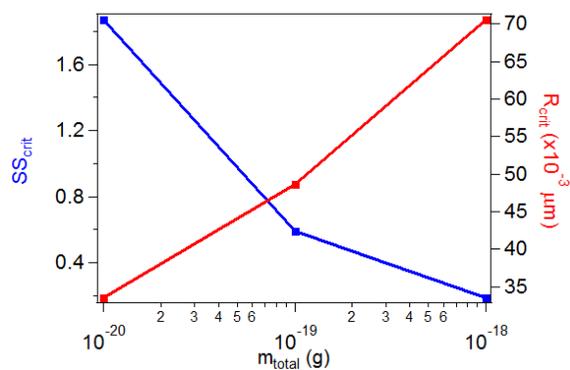
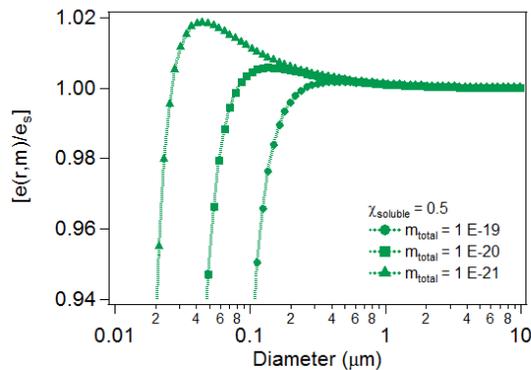
94 The results of the third sensitivity test (Figure 3) were somewhat inconclusive regarding
95 the effect of changing solute identity on critical supersaturation. It was recognized that the trend
96 is dependent on the ratio of i/M_s and not solely on i , thus the critical radius with a higher van't
97 Hoff factor will be larger than a particle with a smaller van't Hoff factor if the molecular weight
98 remained constant. The magnitude of this effect was less significant than those of the other
99 sensitivity tests.

100 The three factors probed in the sensitivity tests can be ranked in accordance to their
101 impact on critical supersaturation and critical radius. The total particle mass has the largest
102 impact, the mass fraction of solute has the second largest impact, and the identity of the solute
103 has the smallest impact. As is consistent with discussions of classical Köhler Theory, the size of
104 the aerosol particle plays the largest role in determining critical supersaturation and critical
105 radius of CCN, although the results show that the presence of insoluble component is significant.
106 Furthermore, studies examining the impact of organic components on CCN activation verify the
107 qualitative trend presented by the second sensitivity test, but quantitative values could not be
108 confirmed¹⁰.

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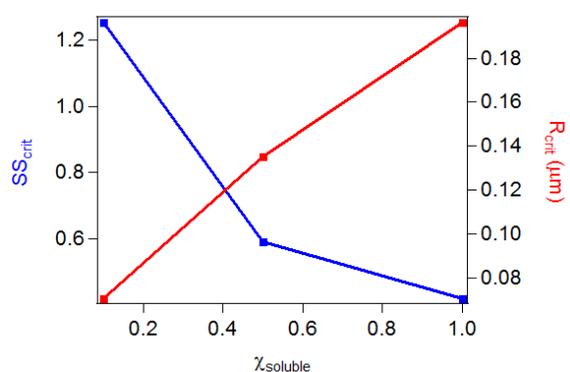
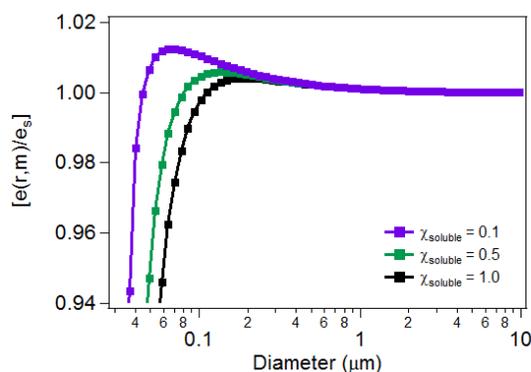
110 **Conclusions**

111 This result is relevant to climate science because almost all aerosols found in nature
112 contain insoluble components. Therefore, models that incorporate the presence of insoluble
113 components in CCN are critical. Furthermore, calculations based on classical Köhler Theory,
114 which does not take insoluble components into account, underestimate the critical
115 supersaturation and overestimate the critical radius of mixed component aerosols. While the
116 modified Köhler equation presented in this model relies on several assumptions and
117 simplifications, the model provides a good starting point for development of further models that
118 take insoluble components of CCN into account.



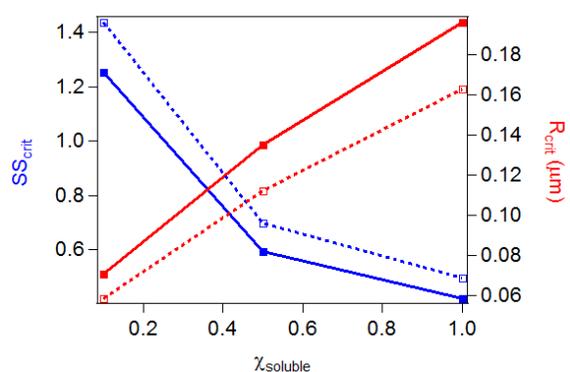
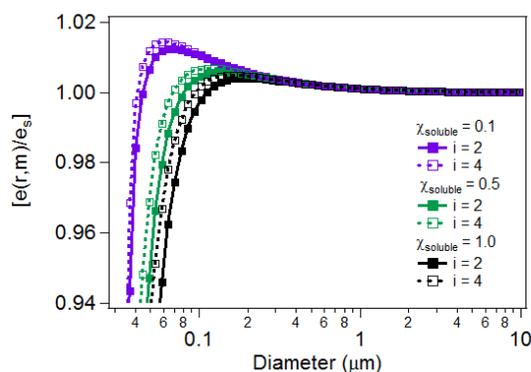
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Figure 1: Saturation ratio as a function of particle diameter for varied total particle mass at a constant mass fraction of soluble component (left). Critical supersaturation and radius for each scenario are taken as the peak maxima (right).



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Figure 2: Saturation ratio as a function of particle diameter for varied mass fraction of soluble component at a constant total particle mass (left). Critical supersaturation and radius for each scenario are taken as the peak maxima (right).



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Figure 3: Saturation ratio as a function of particle diameter for varied van't Hoff factor (solid vs. dashed) and mass fraction of soluble component (left). Critical supersaturation and radius for each scenario ($i=2$, solid; $i=4$, dashed) are taken as the peak maxima (right).

136 **References**

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142 *Comparing Critical Supersaturations: Atmospheric Cloud Condensation Nuclei VS. Known Compounds*

143 **Supplemental Information**

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145 Raoult's Law for an electrolytic solution states that:

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$$\frac{e_s(n_{solt})}{e_s} = 1 - \frac{in_{solt}}{n_{H_2O}}$$
 Equation 4

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149 Since $n = m/M$ and $m = \rho V$ we can state that

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$$n_{solt} = \frac{m_{solt}}{M_{solt}}$$
 Equation 5

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153
$$n_{H_2O} = \frac{V_{H_2O}\rho_l}{M_v}$$
 Equation 6

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155 For the purpose of our model in which an insoluble core is surrounded by an aqueous solution
156 with a solute that contributes minimally to the total volume, we can describe the volume of water
157 as:

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$$V_{H_2O} = V_{tot} - V_i$$
 Equation 7

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160 Using the definition of volume for a sphere, we can write that

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162
$$V_{H_2O} = \frac{4\pi(r^3 - r_i^3)}{3}$$
 Equation 8

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164 where r_i is the radius of the insoluble core. Substituting (5), (6) and (8) into (4) yields

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$$\frac{e_s(n_{solt})}{e_s} = 1 - \frac{3im_{solt}M_v}{4\pi M_{solt}\rho_l(r^3 - r_i^3)}$$
 Equation 9

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168 (9) can be combined with the Kelvin effect to yield the modified Köhler equation:

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$$\frac{e_s(r, n_{solt})}{e_s} = \left(1 - \frac{b}{r^3 - r_i^3}\right) \exp(a/r)$$
 Equation 10