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Atmospheric Processes and their Controlling Influence on Cloud Condensation Nuclei Activity

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Table of Contents

1 Introduction

"If there was no dust in the air there would be no fogs, no clouds, no mists and probably no rain."

- *On Dust, Fogs and Clouds* (1881), John Aitken

As Aitken[1] recognized near the end of the 19th century, particles play a critical role in the atmosphere by serving as seeds from which liquid water droplets (i.e., Aitken's reference to clouds, fogs, mists and rain) initiate and grow. The particles that become cloud droplets via heterogeneous nucleation of liquid water are called cloud condensation nuclei (CCN). CCN, and atmospheric aerosol particles in general, have both primary and secondary sources. Primary sources include direct emissions of sea spray, volcanic aerosol, soot, biomass burning, dust and primary biological aerosol particles, while secondary sources include nucleation of new particles from gas-phase precursors and growth of new or existing particles by gas-to-particle partitioning, heterogeneous chemistry, and multiphase chemistry. The potential for an atmospheric particle to act as CCN, termed its CCN activity, is ranked by the atmospheric water vapor pressure required for it to nucleate into a droplet, and depends on both its size and chemical composition. While there has been debate in the scientific literature as to whether variability in particle size distributions or composition is the stronger influence on the variability in observed CCN activity, we note that these two factors are intrinsically linked: changes in composition often have the effect of changing particle size, and thus the physical processes of particle growth cannot be entirely separated from chemical processes. Multiple chemical and physical processes control the number and activity of CCN particles. For example, coagulation is a physical process in which existing particles collide to form larger particles having different CCN activities, but at the same time, the total number of particles is decreased. Condensation of gases onto particles increases their size and modifies their composition, changing the critical supersaturations and thus the spectrum of CCN activities in the population.

Cloud formation is initiated when the relative humidity of an air parcel is increased above saturation (i.e. 100% relative humidity, RH); two common examples of processes that can supersaturate an air parcel are radiation cooling as occurs in a ground fog, or upward motion, expansion, and cooling as occurs in orographic clouds as air flows over a mountain range. The atmospheric particle generally contains condensed water even at RH < 100%, and these water

contents, typically assumed to be in equilibrium between the particle and gas phases, increase sharply above RH~85%.[2] Equilibrium water contents near RH=100% are so large that the amount of water in the aerosol phase may be limited by the kinetics of the condensation process. As will be explained below, under certain supersaturated conditions (RH > 100%) no stable equilibrium exists, and water will condense without impedence onto existing particles to form cloud droplets. The point at which nonequilibrium droplet growth occurs is defined as the particle's critical supersaturation, which we will refer to as the definition of its "CCN activity".

The interest in the CCN activity of the atmospheric aerosol stems primarily from two important consequences. First, the primary sink of atmospheric submicron particulate matter is removal by precipitation, which largely controls the lifetime of aerosol mass; nucleation scavenging is the main pathway for incorporation into precipitation.[3] Second, CCN exert an influence on their own sink mechanism, since they are critical to fog and cloud formation. Increases in the number concentrations of CCN active at typical stratus cloud supersaturations generate more competition for available water vapor, and can result in a larger number concentration of smaller cloud droplets, which increases the cloud's shortwave reflectivity and thus the cloud albedo radiative effect.[4] This process is exemplified in the observation of ship tracks over the ocean, embedded in the surrounding stratus cloud deck, that are caused by plumes of particles from the ship exhaust that enhanced the in-plume CCN concentrations relative to the surrounding clouds.[5] Through their impacts on the initial droplet size distributions and number concentrations, CCN can also affect precipitation formation. For shallow warm clouds, elevated CCN number concentrations are likely to suppress precipitation formation, with the further effect of increasing cloud lifetime, thus impeding the particulate mass sink process and potentially magnifying the radiative effects.[6] However, dynamical responses of clouds to changes in the microphysical properties induced by elevated CCN concentrations complicate the overall picture, especially at larger spatial scales.[7] These physical processes are the basis for some of the hypothesized aerosol "indirect effects" on climate, as shown schematically in Figure 1, which contrasts CCN levels and their hypothesized impacts on warm, shallow cloud albedo under "clean" (e.g., pre-industrial) and "anthropogenically-influenced" conditions.[8] Figure 1 also illustrates that the number of available CCN is not equal to cloud drop number concentrations, since cloud formation is a dynamic process, and non-polluted regions may have a different radiative response to a change in aerosol loading than do more polluted regions.[9] While studies have been conducted on the effects of variations in CCN number concentrations on convective and other cloud types that

include the ice phase,[10] those linkages are more complex, are highly dependent on cloud type and environment, and are not discussed here. Nevertheless, CCN characteristics must affect global climate by influencing cloud microphysical and radiative characteristics and affect the global hydrological cycle via their role in precipitation formation. However, these effects are poorly constrained and highly uncertain, resulting in large contributions to uncertainties in model predictions of Earth's present and future climate.[11]

A thorough review of the roles of size, composition, and mixing state on the activation of atmospheric particles to cloud droplets, and the resulting impacts on aerosol indirect effects on warm clouds, is provided by McFiggans et al.[12] In particular, that review provides a comprehensive discussion of the basic theory of droplet activation, demonstrates competing effects in the activation of a particle population, and summarizes many of the observational studies available at that time that describe the composition and hygroscopic growth of ambient particulate matter, with a particular focus on the nature of the organic fraction of the ambient aerosol. It also includes a detailed discussion of the potential roles of surfactant films on drop activation and growth. A more recent review by Kreidenweis and Asa-Awuku[2] summarizes the state of knowledge regarding measurement approaches and laboratory and field observations of water uptake by aerosol particles, and its dependence on particle chemical composition, under sub- and super-saturated conditions. The frameworks that describe cloud condensation nuclei have advanced and additional work has been conducted to understand how chemical processes occurring in the atmosphere might modify drop activation behaviors, such that a new review of these physical and chemical processes is warranted. We therefore describe here only briefly, in Sections 2 and 3, the underlying theory and the relationship to the nature of the atmospheric particulate matter that has already been treated in these, and other,[13] reviews. In Section 4 we focus on the connections between the processes that modify particle composition and how these intersect with processes that change particle size, both of which ultimately determine the ability of a given particle to activate into a cloud droplet and thus influence its removal from the atmosphere in precipitation.

2 Fundamentals of Water Uptake by Particles

"The nature of the nuclei of which a cloud is really formed can best be investigated through the droplets of which the cloud is composed. Such an investigation generally presents great difficulty."

- H. Köhler (1936) [15]

2.1 Particle Activation

The equilibrium between the relative humidity in the ambient environment and the vapor pressure over a particle that contains water, is governed by the following equation that relates relative humidity, solubility/composition (or, more accurately, water activity of the pure water or aqueous solution in the particle phase, a_w) and wet particle diameter, assuming sphericity:

$$\frac{RH}{100} = a_w \exp\left(\frac{4\sigma_s M_w}{RT\rho_w D_{p,wet}}\right) \quad (1)$$

where *RH* is the ambient relative humidity (in %), σ_s is the surface tension of the wet particle at the solution/air interface, M_w is the molecular weight of water, *R* is the ideal gas constant, *T* is temperature (in K), ρ_w is the density of water and $D_{p,wet}$ is the (spherical) diameter of the wet particle (or droplet, for particles that have sufficient water content). For pure water at 293 K, $\sigma_s = 72.8 \times 10^{-3}$ N m^{-1}. (Surface tension is often given in the non-SI units of dynes cm^{-1}; 1 dyne cm^{-1} = 10^{-3} N m^{-1}.) In Equation (1) the partial molar volume of water has been approximated by the molar volume of pure water. The equation takes into account the effect of surface curvature on the equilibrium state, which is important for microscopic particles and is termed the Kelvin effect. The Kelvin effect expresses the fact that the vapor pressure over a surface increases with surface curvature. In equation (1), the *RH* is calculated relative to the saturation vapor pressure of water, $p_{w,sat}$, over an infinitely flat plate; in practice, "infinitely flat" can be taken as greater than ~ 1 μm. Since $p_{w,sat}$ is temperature dependent, *RH* is temperature dependent and defined as:

$$RH(\%) = \frac{p_{w,amb}}{p_{w,sat}(T)} \times 100 \quad (2)$$

where $p_{w,amb}$ is the ambient (i.e. observable) vapor pressure of water. The water activity, or water activity of the condensed phase, is defined as:

$$a_w = \frac{p_w}{p_{w,sat}} \quad (3)$$

where p_w is the actual vapor pressure of water over the condensed phase for infinite drop sizes; pure water has $a_w = 1$ by definition. Water activity is discussed further in Section 2.2.

The water contained in the particle phase may be adsorbed water, if the particle surface is such that it supports adsorption; or absorbed water, forming an aqueous solution with at least one of the compounds comprising the dry particle. In early literature, it was stated that the particle needed to have "soluble material" in order to serve as a CCN and the solubilities of various constituents of the atmospheric aerosol were explored. However, this definition is imprecise, as "solubility" refers to the amount of a substance that completely dissolves in a specified amount of water to form a saturated solution; we consider the implications of solubility in Section 2.2.2. More commonly-used in the recent literature is the term "hygroscopicity", which is taken to refer to the mass of water per unit mass of dry particulate matter that is in equilibrium with a specified RH <100%. The Oxford English Dictionary defines hygroscopic as "(of a substance) tending to absorb moisture from the air." In general, the more hygroscopic a material, the higher the equilibrium water content at a given relative humidity; or equivalently, a more dilute solution is required to achieve a specific water activity.

In general terms of interpretation, Equation 1 can be written as follows:

$$\frac{RH}{100} = [water\ activity\ term] \times [Kelvin\ term] \quad (4)$$

The amount of water in the condensed phase at equilibrium must be viewed through the lens of the combination of these two terms. In general, $a_w \leq 1$, and the Kelvin term is always ≥ 1. Starting with a dry particle of a given size and considering only water absorption and formation of an aqueous solution, as RH increases and water is taken up, increasing the particle wet diameter, the a_w increases, monotonically approaching 1 from below, while the Kelvin term decreases, monotonically approaching 1 from above. Below 100% RH there is a single-valued equilibrium relationship between RH and wet diameter. However, the relationships between the water activity term, the Kelvin term and the wet particle diameter lead to a situation where one, *two, or no* equilibrium states are possible, not all of them stable equilibria, for RH values greater than 100%. Often, when the RH is > 100% it is expressed as the percent supersaturation, defined as:

$$s(\%) = \left(\frac{RH}{100} - 1\right) \times 100 \quad (5)$$

A graph of *RH* or *s* as a function of the particle wet diameter gives the well-known Köhler curve,[15] the shape of which depends on the dry particle diameter and the particle composition (Figure 2). Figure 2 illustrates the influence of the Kelvin term and the water activity term in determining the overall Köhler behavior. We note that the ordinate indicates the equilibrium vapor pressures over the droplet at the various wet diameters, and is only equivalent to the ambient water vapor pressure under conditions of equilibrium. If the particle experiences a slight gain (loss) of mass from this initial equilibrium state, the vapor pressure over the particle is decreased (increased).

Figure 2 illustrates an interesting feature of the Kohler curve: there is a maximum in the particle vapor pressure at a particular wet size, and no equilibria exist for ambient relative humidities greater than that value. The supersaturation at this point is called the critical supersaturation (s_{crit}) and occurs at the point where:

$$\frac{ds}{dD_{p,wet}} = 0 \quad (6)$$

The equilibria to the left of s_{crit} are stable equilibria. Assuming a constant ambient environment, the equilibria for larger wet diameters are all unstable equilibria. Any shifts in wet diameter will lead to either unstable growth (if the diameter increases) or evaporation to the size corresponding to the stable equilibrium branch (if the diameter decreases slightly).
Once a particle reaches the size corresponding to s_{crit} it is considered to have activated into a cloud droplet and to be able to grow spontaneously if the atmospheric supersaturation exceeds s_{crit}. The actual value of s_{crit} depends on the particle composition and on its dry size. Typical maximum *s* values achieved in cloud systems range from s_{max} = 0.1-1%, with different cloud types having different typical s_{max} values. Here, values of s_{max} = 0.3% and 1% are used throughout to illustrate differences that might be observed between different cloud system types, and are generally representative of stratocumulus and cumulus cloud systems, respectively.

Figure 3 illustrates how the equilibrium RH calculated from Eq. 1 varies between particles with different initial dry diameters ($D_{p,dry}$) but the same composition. Assuming that water uptake leads to formation of a solution, the smaller the dry particle, the less number of soluble

moles are available for a given wet particle diameter, and thus the a_w is larger. As a result, smaller particles of a given composition activate at larger s_{crit} values. Figure 3B illustrates the general influence of composition on s_{crit}, and ultimately the ability of a given particle to act as a CCN under particular atmospheric conditions. For particles of the same size but different composition, those that are composed of lower hygroscopicity material (such as organics) require larger s_{crit} values to activate compared to those that are composed of higher hygroscopicity material (such as inorganic salts). These two figures together illustrate a key point: although composition dictates the hygroscopicity of a given particle, the ability of a particle to activate into a cloud droplet depends on both composition and size.

In the atmosphere, a given air mass will go through some trajectory in which it reaches some maximum supersaturation, s_{max}. Whether a particle in that air mass will activate depends on the s_{crit} value for that particle relative to the s_{max}. A particle might be highly hygroscopic, but if it is too small it may not activate. Similarly, a particle might be comprised of very low hygroscopicity material, but if it is sufficiently large it may still activate. As such, s_{crit} is the fundamental parameter that describes the CCN activity. Figures 4a,b illustrate the relationship between s_{crit}, particle dry diameter and particle hygroscopicity, and demonstrate that to maintain activity at a selected critical supersaturation, larger percentage changes in hygrosopicity are required than percentage changes in diameter. These figures thus demonstrate that the sensitivity of CCN activity to fractional changes in particle size is greater than the sensitivity to fractional changes in composition, as expressed via the κ parameter. This observation is consistent with McFiggans et al.[12], who calculated the relative sensitivity of drop number concentration to be greater for changes in the particle radius than for changes in the soluble mass fraction of the dry particle.

The above discussion focuses on the supersaturation that is required for a certain particle to reach its critical size and activate into a droplet. In the atmosphere, supersaturation is generated by the cooling of an air parcel radiatively, as in a ground fog; via adiabatic expansion as it is lifted to higher altitudes, as in a convective cloud; or by constant-pressure, adiabatic mixing of air parcels, as in a contrail. Although a detailed discussion of the physics of cloud formation and evolution is beyond the scope of this review, a brief mention of how particles interact with an evolving supersaturation field is in order. As explained in detail by McFiggans et al.[12], as soon as the first particles are activated into cloud drops and begin to grow by condensation of water vapor, a competition arises between the rate of generation of supersaturation and the rate of scavenging of supersaturation via nucleation of new droplets and condensational growth of

the droplet population. This competition results in transient behavior where initially the supersaturation rises faster than it can be relieved by vapor scavenging, but subsequently the rates approximately balance, and for continued drop growth, the rate of vapor scavenging dominates and the ambient supersaturation declines. The conditions where the rates are approximately equal define the peak supersaturation in that parcel, which is generally achieved close to cloud base. Rates of vapor scavenging increase with the number concentrations of particles capable of serving as CCN at supersaturations equal to or lower than the peak. As a result, the peak supersaturation depends in a complicated way on the CCN number concentrations, and increases in total particle number concentrations do not always result in similar increases in cloud droplet number concentrations.[12,16]

The peak supersaturation is clearly a quantity of interest in understanding aerosol indirect effects on clouds. It is currently not directly measurable but has been deduced from other measurements (e.g., Noble and Hudson, 2013; Kruger et al., 2014; Hoppel et al., 1986).[17] Peak supersaturations in stratus clouds are generally assumed to reach ~0.3%, whereas in convective clouds this maximum can exceed 1% and in fogs may be much lower. The notion that a few particles with low critical supersaturations may serve as effective condensational sinks even at very low supersaturations, rapidly growing to sizes exceeding 20 μm and thereby initiating drizzle formation in clouds, has given rise to the term "giant CCN" for such particles. This term appears to have been used first by Levin et al.[18] to describe dust particles coated with sulfate that were observed in field studies in the eastern Mediterranean. As can be readily seen in Figure 4, a 500 nm particle need have only a low volume fraction of highly hygroscopic material, sufficient to result in an overall $\kappa \sim 0.01$, to readily activate at $s \sim 0.1\%$; indeed, supermicron particles need only be wettable ($\kappa \sim 0$) to activate at low supersaturations. The impacts of giant CCN on precipitation formation have been studied in a variety of models [19] and some observations exist pointing to their likely existence in certain locations.[20] The potential role of biologically-derived particles such as pollen as giant CCN has also been postulated.[21]

2.2 Water Activity

2.2.1 Water absorption

Water activity is a critical determinant of whether a wet particle of a given size will be able to overcome the Kelvin effect at a given *s* and activate into a droplet. As noted above, p_w (and thus a_w) is affected by the presence of solutes in water. Water activity is a measure of effective concentration, as it accounts for non-ideal chemical interactions between the solute and its surroundings, e.g. other solute molecules. If absorption is the controlling mechanism and if the compounds being considered are completely soluble at the point of activation, then in the case where non-ideal interactions are negligible and for a non-volatile solute (such as most inorganic salts) the water activity is essentially equal to the mole fraction of water. For a single component system, the water activity can be calculated as:

$$a_w = \frac{n_w}{\nu n_s + n_w} = \frac{1}{1+\frac{V_s}{V_w}\cdot\frac{\nu\rho_s M_w}{\rho_w M_s}} = \frac{1}{1+\frac{D_{p,dry}^3}{D_{p,wet}^3 - D_{p,dry}^3}\cdot\frac{\nu\rho_s M_w}{\rho_w M_s}} \quad (7)$$

Equation 7 is essentially a statement of Raoult's law. In Equation 7, subscripts *s* and *w* refer to solute and water, respectively, n_x is the number of moles, ν is nominally the number of ions at full dissociation, V_x is the volume, ρ_x is density and M_x is molecular weight. It should be noted that the V_s refers to the volume of species that are in solution, which might be different than the volume of the dry particle. The right-most expression in Equation 7 assumes volume additivity, spherical particles, and $V_s = V_{p,dry}$. For a multi-component system, Equation 7 can be expanded as

$$a_w = \frac{n_w}{\sum_i \nu_i n_{s,i} + n_w} = \frac{1}{1+\frac{M_w}{V_w \rho_w}\left(\sum_i \frac{\nu_i V_{s,i} \rho_{s,i}}{M_s}\right)}\ , \quad (8)$$

Equations 7 and 8 indicate that, neglecting surface tension effects, the number of dissolved moles is the key determinant of whether a given particle will activate into a droplet. For most inorganic salts, water activity for any solution composition can be accurately calculated using models such as the Aerosol Inorganics Model (AIM), [22] ISORROPIA [23] and EQUISOLV II, [24] among others. Conceptually, water activity for aqueous solutions of organic species can be understood in a similar manner as the inorganic solutes, but where dissociation may not play a

role, depending on structure. The activity of mixed inorganic-organic solutions can also be calculated using, for example, Extended AIM (E-AIM) [25] or AIOMFAC.[26]

Alternatively, empirical or semi-empirical models can be used to parameterize the relationship between a_w and dry and wet particle diameters.[27] Many of these empirical representations attempt to reduce the system complexity to a single descriptive parameter. Equation 7 is the basis for one such parameterization, where the ν term is treated as an adjustable parameter and is provided as a function of composition to account for non-ideal interactions.[28] An alternative, widely-used parameterization[29] is rooted in Equation 7, but groups together the density, molecular weight and dissociation terms into a single parameter, κ, with:

$$\frac{1}{a_w} = 1 + \kappa \frac{V_{dry}}{V_w} \tag{9}$$

where V_{dry} is the volume of dry particle, which is essentially equal to V_s in Eqn. 7. Plugging Equation 9 into Equation 1, and assuming spherical particles, one obtains:

$$\frac{RH}{100} = \frac{D_{p,wet}^3 - D_{p,dry}^3}{D_{p,wet}^3 - (1-\kappa) D_{p,dry}^3} \exp\left(\frac{4\sigma_s M_w}{RT\rho_w D_{p,wet}}\right) \tag{10}$$

The parameter κ is termed the hygroscopicity parameter and is compound specific; more hygroscopic compounds have larger values of κ and less hygroscopic ones have smaller κ values. A value of κ = 0 corresponds to a nonhygroscopic, but perfectly wettable, particle (a_w = 1 for all compositions). For mixed component particles, volume additivity of the water contents of individual components according to the Zdanovskii, Stokes and Robinson (ZSR) approximation is typically assumed, leading to[29]

$$\kappa_{avg} = \sum_i \epsilon_i \kappa_i \tag{11}$$

where ε_i is the volume fraction of the individual component *i*. Mixing of components with differing hygroscopicity results in changes to κ and thus the ability of a particle of a given size to activate. However, most atmospheric processes that lead to mixing of different components, or chemical transformations of individual particles, also result in changes in particle size. It is

important to realize that all parameterizations of water activity are independent of particle size, and thus only represent half of the picture needed to characterize the overall ability of a given particle to activate into a droplet; s_{crit} provides a true measure of "CCN activity".

2.2.2 Solubility Limitations

The above formulations for the relationship between s_{crit} and dry diameter assume that the dissolving compounds are completely soluble at the point of activation, and that any insoluble components do not contribute to water uptake. If, however, there some partially soluble compounds within a particle, then the classic Köhler theory must be modified.[12,30] For a partially soluble compound the actual extent of dissolution is a function of the particle water content, and thus of RH and *s*. One method of accounting for solubility limitations retains the single parameter framework of Equation 10, but extends the definition of κ to include solubility as:

$$\kappa^* = \sum_i \epsilon_i \kappa_i H(x_i)$$
$$x_i = \left[\left(\frac{D_{p,wet}}{D_{p,dry}}\right)^3 - 1\right] C_i/\epsilon_i \qquad (12)$$
$$H(x_i) = \begin{cases} x_i \; if \; x_i < 1 \\ 1 \; if \; x_i \geq 1 \end{cases}$$

where ε_i is the volume fraction of an individual dry component *i* and C_i is the solubility of the solute in water in volume of *i* per unit volume of water. For a compound with no solubility limitation ($C_i = \infty$) there is continuous uptake of water at all RH. For species with limited solubility there is no water uptake until the deliquescence relative humidity (DRH) is reached, after which point water uptake is continuous. If the compounds comprising a particle are not sufficiently soluble then deliquescence may only be reached under supersaturated conditions. Under such conditions, it is possible that solubility actually controls cloud droplet activation, as illustrated in Figure 5a. When the supersaturation required to achieve deliquescence is greater than that to achieve activation assuming infinite solubility then the particle activation can be considered under solubility control. There is some interdependence of hygroscopicity and solubility in terms of the critical range over which solubility limitations can have a major influence on activation, and this range depends on the dry particle size, but in general if compounds have $C_i < 0.1$ then solubility may be important to consider. However, in multi-

component mixtures it is possible that the presence of even small amounts (a few percent) of highly soluble material can alter the effective critical supersaturation[31] by moving the system from being solubility controlled to being determined by hygroscopicity and particle size. This is illustrated in Figure 5b, which shows curves for a two-component system, where the two components differ in terms of both their solubility and hygroscopicity. Particle hygroscopicity is often assessed from measurement of the s_{crit} value required to activate particles of a given dry diameter. As such, solubility limitations can lead to a situation where an effective or apparent κ value is derived that is indicative of the combined influences of solubility and hygroscopicity, as opposed to being simply a characterization of hygroscopicity. Consequently, changes in solubility that result from chemical oxidation can be misinterpreted as changes in hygroscopicity.

Solubility considerations are, at least in theory, particularly important for organic compounds, and there have been some suggestive experimental results.[31-32] For example, one study investigating the influence of heterogeneous oxidation (Section 4.1.2) of initially non-hygroscopic, effectively insoluble organics found that quantitative explanation of the CCN activity of the resulting particles required treating the particles an evolving distribution of non- and partially soluble compounds[33]. Such behavior is understandable given that organic solubility is reasonably correlated with the extent of oxygenation, which can be characterized by the oxygen-to-carbon atomic ratio. Organics with O:C < 0.2 can be considered effectively insoluble, those with O:C > 0.6 effectively infinitely soluble and those with 0.2 < O:C < 0.6 as partially soluble.[34]

2.2.3 Water adsorption

There has been increasing interest in the potential role that water adsorption can play on the ability of a given particle to activate. Water adsorption may be important for insoluble particles, which can include dust[35] or black carbon, [36] and may be the initial mechanism for water uptake by crystalline and semi-solid particles,[37] potentially including organic-dominated aerosols. In adsorption, water molecules bind to the surface of a particle, which acts as a substrate, with some interaction energy that is a characteristic of the chemical identity of the substrate. Once a monolayer is formed, subsequent water molecules can bind to the surface-bound water molecules with a different interaction energy, forming a multilayer. As the multilayer increases in thickness, the nature of the chemical interactions evolves towards that of pure water,

assuming that there are no solutes present in this layer. By definition, this pure water multi-layer will have an activity of unity. Because the activity of this thin layer is so large, for a dry particle of a given diameter the Kelvin effect can be overcome at a smaller wet particle diameter than compared to an equivalently-sized soluble (absorptive) particle. One challenge in characterizing and quantifying the role of adsorption in CCN activation is that small amounts of soluble materials can modify the dominant mechanism from adsorption to absorption and thus will have a strong influence on the observed water uptake.[38]

It has been suggested that the Frankel, Halsey and Hill (FHH) multi-layer adsorption isotherm is appropriate for atmospheric particles near activation.[39] The FHH isotherm takes the form:

$$a_w = \exp\left(-\frac{A_{FHH}}{\Theta^{B_{FHH}}}\right) \quad (13)$$

where A_{FHH} and B_{FHH} are experimentally-determined fit parameters and Θ is the surface coverage of water molecules. The parameter A_{FHH} is related to the strength of interaction between water molecules adsorbed in the first monolayer and the substrate (i.e. particle) surface. B_{FHH} characterizes the strength of longer range interactions between the substrate surface and adsorbed water molecules in subsequent layers, with smaller values of B_{FHH} corresponding to a greater distance over which attractive forces act. The values of A_{FHH} and B_{FHH} are specific to the particular definition used for Θ. It has been suggested that Θ for application to atmospheric particles is characteristic of the number of adsorbed water layers,[39] with

$$\Theta = \frac{D_{p,wet} - D_{p,dry}}{2D_{water}} \quad (14)$$

where D_{water} is the assumed diameter of a water molecule (~2.75 Å). Since the wet particle diameter at activation is expected to be smaller for nucleation that proceeds via adsorption relative to absorption, measurements of the size of the droplet at or near activation might help to elucidate which process dominates the activation process.[40]

The sensitivity of a_w, and ultimately s_{crit}, to either A_{FHH} or B_{FHH} is illustrated in Figure 6, which shows the variation in s_{crit} with B_{FHH} for various A_{FHH}. For B_{FHH} in the range ca. 0.7 to 1.3 there is a relatively strong dependence on A_{FHH}, but at larger B_{FHH} values the dependence on A_{FHH} is small. Certain combinations of B_{FHH} and A_{FHH} do not yield a well-defined maximum in a graph

of *s* versus wet diameter, in particular when B_{FHH} is small (B_{FHH} < ~0.7; Figure 6), which would indicate that under these conditions the particles do not actually activate but instead continuously take up water. Whether such small B_{FHH} values, which imply relatively strong interactions between the substrate surface and adsorbed water molecules, correspond to physically realistic situations for atmospheric particles has not been established, although seems unlikely.[39] Recent lab studies of aerosols dry generated from soil samples suggest that appropriate parameters for representing typical lofted desert dusts are A_{FHH} ~2.25 ±0.75 and B_{FHH} ~1.2 ±0.1.[35b]

2.3 Surface tension

Equation 1 indicates a potentially important role for surface tension in determining the likelihood of activation for a given particle. As surface tension decreases, the Kelvin term decreases in magnitude, thus leading to a smaller s_{crit}. Although it is clear that surface tension can affect s_{crit}, there has been longstanding debate as to the extent that it actually does so in the atmosphere.[41] Aqueous solutions of many inorganic salts actually have surface tensions that are slightly larger than that of pure water, but the influence decreases in magnitude as the wet particles (or droplets) grow, thus diluting the salt concentration. Surface-active compounds, typically organics, can, however, decrease the surface tension of water substantially, leading to activation at lower s_{crit}. Analyses of fog and aerosol samples from both ambient and laboratory samples have shown the potential for organics to decrease the surface tension of water.[41-42] However, as the wet particle grows the concentration of the surface-active compound decreases along with the effect on the surface tension, thus indicating that the influence of surfactants on CCN activation is a dynamic process. The variation in surface tension with the bulk concentration of a surface active species (c, mol m^{-3}) tends to follow the Szyskowski-Langmuir adsorption isotherm:[43]

$$\sigma_{obs} = \sigma_w - RT\Gamma_\infty \ln\left(1 + \frac{c}{a_L}\right) \quad (15)$$

where σ_{obs} is the actual (observable) surface tension, σ_w is the surface tension for pure water, R is the ideal gas constant, T is temperature, a_L is the concentration at half surface coverage (mol m^{-3}) and Γ_∞ is the maximum surface excess (mol m^{-2}). Typically, adsorption isotherms are developed from measurements made on macroscopic solutions, but there may be some

differences in microscopic droplets, which have large surface area-to-volume ratios. As surface-active compounds are partitioned to the surface their bulk concentration (i.e. solubility effect) decreases, thus partially offsetting the surface tension depression.[44] If the decrease in bulk concentration is substantial it can also lead to deviations from Eqn. 15,[33,45] and there may additionally be effects imposed by ordering of surfactants at the air-water interface.[46] In general, lower hygroscopicity materials have smaller wet particle diameters at activation, for a given $d_{p,dry}$ (Figure 3B). This smaller size corresponds to larger concentrations of the dissolved components, which are diluted as the wet particle grows. As such, the largest influence of surfactants on CCN activity is found for particles that are mostly organic (i.e., less hygroscopic),[47] although surfactants can influence particles that are mostly inorganic.[48] For more information on the role of surfactants in aerosols, the reader is referred to the discussion in McFiggans et al.[12] and the more the recent review by McNeill et al.[49]

3 Particle Size, Composition and CCN Activity

The above discussion illustrates that the critical supersaturation of a given particle, and thus the likelihood that that particle can activate into a cloud droplet under particular conditions, is dependent upon both particle size and composition. Particle concentrations and the shapes of size distributions vary with location, and depend on the proximity to varying particular sources and subsequent atmospheric processing. This is shown in Figure 7, which presents particle size distributions measured during a variety of different field campaigns. The various measurements were made at terrestrial urban (DISCOVER-AQ in Fresno, CA, USA and ClearFlo in Detling, UK[50]) and rural (SOAS in Look Rock, TN, USA and AMAZE in the central Amazon of Brazil[51]) locations, and in the marine boundary layer in urban-influenced (CalNex in the CA coastal region[52]) and more remote (ACE-1 in the southern Pacific Ocean[53] and ICEALOT in the north Atlantic Ocean[54]) locations. It is evident that the nature of the distributions differs between each location with, perhaps unsurprisingly, the greatest similarity between the two remote marine distributions. Independent of composition, differences in the size distributions play an important role in determining the fraction of particles that will activate into cloud droplets under particular conditions – the fraction of particles with s_{crit} below some value, as also discussed in detail by McFiggans et al.[12] Under the overly simplistic assumption that all particles in a given size distribution have the same composition or κ value, the cumulative number of particles that have s_{crit} values below a given value can be visualized for the distributions in Figure 7. Figure 8 shows such cumulative distributions for three different

assumed κ values, corresponding to particles with low, medium and high hygroscopicities. The fraction of total particles that would activate below s = 0.3% and 1% can be taken as representative of particles that might activate during formation of stratocumulus clouds and warm cumulus clouds, respectively. For a given κ, it is clear that there can be substantial differences between the distributions in terms of the fraction of particles that would activate during formation of these different cloud types. Changes in κ lead to clear and substantial shifts in the fraction of particles that would activate at a given s, but do not dramatically alter the relative sensitivity of the activated fraction to the nature of the size distribution. Understanding the manner in which various atmospheric processes lead to modifications in particle size and in particle composition—and how these are interrelated—are critical to understanding the global distribution and impacts of CCN.

4 Influence of Atmospheric Processes on CCN Activity and Number Concentration

Both chemical and physical processes control the size and chemistry of atmospheric aerosol particles, and changes in these properties thus allow a particle to change its critical supersaturation. Here, we consider how these processes affect the ability of particles to act as CCN.

4.1 Chemistry

Ageing of atmospheric trace gases and particles occurs through oxidation reactions, and typically results in molecules with higher oxidation states, through a combination of fragmentation and functionalization processes.[55] Oxidation causes an increase in valence state of a given chemical species, and typically occurs in the atmosphere via reaction of molecules with oxidants, including hydroxyl (·OH) radicals, nitrate ($\cdot NO_3$) radicals and ozone (O_3). Functionalization occurs when these oxidation reactions result in the addition of oxygen and other atoms to a molecule, and constitute a change in chemical functional group – for example, the addition of an alcohol (-OH) or carboxylic acid (-C(O)OH) group. The addition of oxygen atoms to a molecule is more specifically referred to as oxygenation. Fragmentation occurs when the oxidation reaction creates an unstable molecule that decomposes and breaks apart to form smaller product(s) than the original parent molecule. Molecules with more functional groups often have lower vapor pressures, while smaller molecules typically have higher vapor pressures, than their parent molecule. Molecules emitted into the atmosphere typically undergo

multiple oxidation reactions, and ambient air simultaneously contains multiple generations of oxidation reactions. These processes occur in both the gas and particle phases, which interact through condensation or evaporation of gas-phase vapors onto or from particle surfaces, exchange of material between phases via displacement reactions, and heterogeneous and multiphase chemical reactions that can include in-cloud (aqueous phase) production of new particle material.[56] Each of these processes can change size and hygroscopicity, and thus the particle's critical supersaturation. Figure 9 summarizes the net effects of atmospheric chemistry processes on CCN activity through particle shifts within a dry diameter-critical supersaturation space.

4.1.1 Gas-particle phase partitioning

Gas-particle phase partitioning, or exchange of semi-volatile gases between the atmosphere and particulate matter, can both change particle size and change particle hygroscopicity. Irreversible condensation of low-volatility gases, such as sulfuric acid, has long been recognized as an important particle growth mechanism. Volatile inorganic compounds can also partition to the particle phase: ammonium nitrate (NH_4NO_3) exists in thermodynamic equilibrium with ammonia (NH_3) and nitric acid (HNO_3) gases, and the equilibrium can have substantial impact on aerosol mass and size along thermal gradients.[57]

Gas-particle phase partitioning is also an important process in the formation of secondary organic aerosol, in which emitted gas-phase compounds are oxidized in the atmosphere and partition to the particle phase.[58] Traditionally, gas-particle partitioning of organic compounds has been considered an almost instantaneous equilibrium process, governed solely by thermodynamics and it is typically assumed that such partitioning is reversible. However, if the volatility of the condensing products is sufficiently low then the overall process can be considered effectively irreversible. This has implications for the concentrations of CCN in a given region because irreversible growth occurs proportionally to surface area, whereas reversible partitioning means that new mass will be distributed according to particle volume.[59] Thus, the growth of particles in a given size regime depends on the nature of the partitioning process, as well as the speed with which multiphase processes transform condensed organics (Section 4.1.3). Additionally, recent studies indicate that organic particles can be highly viscous semi-solids,[60] suggesting that kinetic limitations in gas-particle partitioning may be atmospherically relevant. However, the phase-state of pure organic and mixed organic/inorganic particles is dependent on water content, with particles exhibiting

increasingly liquid-like properties as RH increases,[61] and sometimes phase-separation[62] as RH decreases.

While both inorganic and organic compounds condensing on aerosol surfaces will cause aerosol growth and thus decrease critical supersaturation, the extent of this impact depends on the difference in composition between the parent aerosol and condensing vapors. The addition of non-hygroscopic material will serve to decrease critical supersaturation solely through increases in particle size, while the addition of the same amount of highly hygroscopic material will decrease critical supersaturation even further by affecting both size and hygroscopicity. The relative importance of gas-particle partitioning on CCN activity depends on the nature of the condensable material: for example, the condensation of inorganic acids onto existing particles will typically have a more substantial impact on lowering s_{crit} than the condensation of organic molecules.

The presence of multiple species in the gas-phase results in the likely simultaneous co-equilibration and co-condensation of multiple gas-phase species to a particle at the same time. This co-condensation has been shown to decrease s_{crit} for multiple organic compounds,[63] and for inorganic systems of nitric acid and ammonia.[64] Co-condensation of multiple organic gases to a particle surface also serves to increase the number of cloud droplets, an effect that increases as temperature decreases. Further, an increase in particle mass of one organic component serves to enhance condensation of other components, as does the increase in particle liquid water content.

Of course, gas-particle partitioning does not move mass only from the gas-phase to the particle phase. Evaporation, whether resulting from dilution, temperature increases or chemical reactions, can decrease particle size. Evaporation and shrinkage of particle size is most evident in biomass burning plumes as they are diluted with cleaner background air,[65] where semivolatile organic species shift from the particle to the gas phase to maintain equilibrium.

4.1.2 Heterogeneous chemistry

Heterogeneous chemistry refers to reactions on the surfaces of aerosol particles. This includes reaction and uptake of inorganic compounds, such as N_2O_5, and reactions of oxidants with particle-phase organic molecules. The uptake of trace gases is separate from gas-particle partitioning, as uptake is not governed by thermodynamic equilibrium, but by chemical reactions on the particle surface.[66] The uptake of trace gases is often dependent on particle water content, and thus the influence of heterogeneous reactions on particle hygroscopicity is

linked to the initial particle hygroscopicity.[67] In understanding the role that heterogeneous chemistry plays in altering s_{crit} for a given particle, it is important to distinguish between those processes that tend to both add mass and affect composition and those that primarily only influence composition. Uptake of species such as N_2O_5 can lead to substantial increase in particulate mass, in this case of particulate nitrate, leading to changes in both size and composition.

Heterogeneous reactions between oxidants and particle-phase organics can have a substantial impact on composition. For example, heterogeneous oxidation reactions lead to changes in organic aerosol mass and composition[55a,68] and may affect particle hygroscopicity,[42b,69] potentially by modifying surfactant properties.[33] In addition, the solubility of organics can also be altered by heterogeneous oxidation,[33] which can also impact droplet activation if the parent or product organics are only sparingly soluble (Section 2.2.2). The influence of such reactions on particle size through either mass addition from oxygen incorporation or mass loss from fragmentation and subsequent volatilization of the reaction products is dependent upon the starting organic composition and extent of oxidation.[55a,70] In general, fragmentation reactions become increasingly important as the oxygen content of the organic material increases (i.e. when the particle organics are highly functionalized)[71] and can potentially have substantial impacts on particle mass and size on multi-day ageing timescales.[72] The state of knowledge of reactive surface uptake of trace gases was reviewed extensively by Kolb et al.[66] These authors provide a summary of oxidation experiments that observed a wide range of impacts leading to effects on particle CCN activity, ranging from fragmentation and loss of mass to the gas phase, to formation of more hygroscopic species that remain in the particle phase.

4.1.3 Multiphase chemistry

Multiphase chemistry refers to the uptake of gases into aerosol particles (or cloud droplets) and subsequent reaction;[56] products may be retained in the particle phase or released to the atmosphere. Examples of relevant oxidation reactions occurring in the condensed phase include aqueous oxidation of inorganic molecules (e.g., SO_2 oxidation to sulfate by ozone or H_2O_2) and oxidation of organic molecules.[73] For organic molecules, these oxidation reactions can result in either functionalization, fragmentation or oligomerization, and can sometimes be difficult to disentangle from heterogeneous processes. The impact of these reactions on hygroscopicity depends on the chemical process and on the resulting molecular size and functional groups. In general, if the resulting molecules are neither too volatile nor too insoluble, functionalization

through oxygenation leads to more hygroscopic compounds,[74] and may also produce more surface-active molecules that enhance CCN activity.[75] The most dramatic impact of functionalization on CCN activity occurs for the addition of hydroxyl (-OH) groups, which exceeds the sensitivity of hygroscopicity to addition of carboxylic acid or hydroperoxide ether groups.[74b] However, the addition of nitrate ($-ONO_2$) or methylene ($-CH_2-$) groups has the opposite effect, resulting in decreases in particle hygroscopicity and/or solubility. The addition of methylene groups is an unlikely chemical pathway during oxidation, but the addition of nitrate groups can occur in polluted regions.

Smaller molecules that are produced from multiphase reactions are typically more volatile than their larger counterparts, and more likely to partition from the particle to the gas phase unless stabilized through additional chemical interactions. For example, oxalic and formic acids are common end products of aqueous-phase oxidation, but can be retained in the particle phase if cations are present. Thus, fragmentation has potential impacts on hygroscopicity, volatility, and particle size. Such complex effects have been observed in, for example, the production and volatilization of formic acid from palmitic acid aerosol+OH reactions,[76] and outgassing of methanol, acetaldehyde, formic acid and other volatile organic compounds following uptake of OH radicals by biomass burning aerosol.[77]

Oligomerization is the formation of higher molecular weight compounds from a few monomers. Oligomers have chemical and physical properties different from the original parent molecules, including substantially lower volatilities.[78] Thus, oligomerization shifts the equilibrium of semi-volatile organic compounds, driving molecules from the gas to the particle phase and increasing SOA mass (and particle size), thereby decreasing the critical supersaturation. If oligomerization is fast compared to typical gas-particle partitioning timescales (minutes) then it can also influence the overall way in which a given size distribution evolves because it converts compounds that might, if given sufficient time, be distributed according to particle volume to compounds that condense according to surface area. Oligomers potentially account for over 50% of SOA mass,[78b,79] although the exact contribution of oligomers continues to be an active area of discussion. Oligomerization generally occurs as a volume reaction either within the particle, or through aqueous-phase chemistry in cloud droplets that form SOA upon evaporation.[79a,80] Three key SOA oligomers include (i) peroxyhemiacetals from hydroperoxide + carbonyl reactions, (ii) hemiacetals from carbonyl + alcohol reactions or gem-diols (produced from carbonyl hydrolysis), and (iii) esterification from carboxylic acid + alcohol reactions.[81] Additionally, aldol condensation, acetal formation

from hemiacetal + alcohol reactions, and polymerization from carbonyl + gem-diol or carbonyl + hemiacetal reactions have been proposed to produce oligomers.[78a] Sulfuric acid + alcohol reactions similarly produce higher molecular weight organic sulfate compounds.[58b,82] The relevance of oligomerization to hygroscopicity depends on the net impact of these reactions. Acidic solutions enhance many of these reactions, and aerosol pH can have a substantial impact on the extent of this growth through acid-catalyzed reactions, and by controlling the 'salting in' of organic and inorganic molecules. While these salting-in processes may lower the critical supersaturation of particles, the effect on particle size is likely minor. Overall, the effect of organic multiphase reactions on CCN activity depends on the relative role of functionalization (slight particle growth and usually an increase in hygroscopicity) versus fragmentation (particle shrinkage, indeterminate effect on hygroscopicity).

Ion displacement reactions between gas-phase molecules and the particle surface have a negligible influence on particle size, but do change composition and potentially hygroscopicity. For example, condensation of secondary organic aerosol on sea spray (e.g. chloride-containing) particles in plumes can lead to chloride displacement, wherein weak organic acids displace particle phase chloride as $HCl_{(g)}$ and thus decrease the particle's overall hygroscopicity[83] because the resulting ionic species are less hygroscopic than the original halide salt. Multiphase reactions between oxalic acid and inorganic salts, especially divalent salts, have also been shown to produce organic salts with substantially depressed hygroscopicities.[83b] Chloride can similarly be displaced by nitrate,[84] and since the hygroscopicity of $NaNO_3$ is less than that of NaCl[29] the particle's overall hygroscopicity is decreased, although not to the same extent as for displacement by organic acids.

If aerosol, cloud or fog droplets are not removed by deposition or precipitation, the resulting residual particles that are released to the atmosphere upon evaporation of the water will have s_{crit} values that are lower than the original, unprocessed particle as a result of both an increase in particle size and, most likely, an increase in hygroscopicity that results from reactions in the aqueous phase. The effect can be particularly pronounced in cloud and fog droplets because of the relatively high concentrations of condensed water that serve as reaction volumes and that can absorb and react relatively large masses of vapor; repeated cycling of air through marine stratus clouds has been shown to create bimodal aerosol size distributions, where the particles that served as CCN gained enough mass via aqueous-phase chemical reactions to grow into a distinct mode separated from the initial monodisperse population.[85] Thus, cloud or fog processed particles are likely to activate more easily in the next cloud cycle. In contrast, if

particle scavenging does occur, the remaining, residual particles in the airmass will constitute particles that did not activate into cloud or fog droplets, likely because the s_{crit} of these non-cloud processed residual particles was higher than those that did activate. As such, the next cloud cycle may require a higher supersaturation for initiation of drop formation.

4.2 Condensational growth

The main way in which existing particles grow in the atmosphere is through condensation of low-volatility materials. This growth naturally leads to a decrease in the s_{crit} for a particle, regardless of the hygroscopicity of the condensing material. This is an important aspect of condensational growth in that even if the material added causes a particle to become overall less hygroscopic, the particle does not become a less efficient CCN. However, condensing species are typically at least somewhat hygroscopic and therefore condensational growth represents an addition of $\kappa > 0$ material to the particle, which leads to a further decrease in s_{crit} over that realized from the diameter increase alone. If the condensing species acts as a surfactant and decreases the surface tension of the growing droplet, s_{crit} will be further reduced. Thus condensational growth always acts to decrease s_{crit}.

The influence of condensational growth on s_{crit} is illustrated in Figure 10, where initial particles of either 40 nm (Panel A) or 80 nm (Panel B) grow due to addition of material that is of low (κ = 0.01), moderate (κ = 0.15) or high (κ = 0.67) hygroscopicity onto particles with varying hygroscopicity. The high hygroscopicity case reflects the addition of typical inorganic salts and acids, such as $(NH_4)_2SO_4$, NH_4NO_3, HNO_3 or H_2SO_4.[2,29] The moderate hygroscopicity cases reflect growth due to condensation of secondary organic aerosol (SOA). SOA is not a single, well-defined entity, instead being a mixture of many individual organic compounds. As such, the hygroscopicity of SOA is variable, a reflection of the variability in the individual component hygroscopicities.[74] There have been various estimates of an effective κ for SOA (in practice, for that component of OA identified as being "oxidized") from ambient observations. These estimates come from determination of the κ value for SOA that yields closure between calculated and observed subsaturated hygroscopic growth factors or CCN activity at a given supersaturation. Most such estimates give values in the range ~0.1-0.2, with some indication that the exact value is related to the degree of oxygenation.[86] Surveys of κ values for individual organic molecules detected in the atmospheric aerosol also generally find values in this range, as long as the molecule is sufficiently soluble.[87] The low hygroscopicity case is considered as

a limiting case, as there are few chemical pathways that will lead to growth from direct condensation of such low hygroscopicity materials (although it should be noted that particular multiphase reactions of the condensed organics can depress hygroscopicity).

In all cases, the addition of new material leads to a decrease in s_{crit} (Figure 10a,b). Addition of highly hygroscopic material leads to more rapid decreases in s_{crit} than addition of low hygroscopicity material. The steepness of the decrease (i.e. the change in s_{crit} per nm of growth) is additionally dependent upon the hygroscopicity of the original particle, with more rapid declines in s_{crit} for initially less hygroscopic particles. For initially highly hygroscopic particles, the addition of low hygroscopicity material leads to only small changes in s_{crit} per nm of growth. For example, for an initially highly hygroscopic 40 nm particle there is almost no change in s_{crit} when material with $\kappa = 0.01$ is added until $d_{p,dry}$ exceeds ~110 nm. In contrast, addition of even very small amounts of highly hygroscopic material to initially low hygroscopicity particles leads to large changes in s_{crit}. This can be understood by looking at the dependence of s_{crit} on κ for a given particle size (Figure 10c). When κ is small (< ~0.2), s_{crit} is highly sensitive to small changes in κ, especially for smaller particles, while the dependence of s_{crit} on κ is much weaker when κ is large. This point is also emphasized by the volume mixing rule (Equation 11), which shows that adding small volume fractions of a highly hygroscopic material to a κ=0 particle rapidly increases the mixture κ.

4.3 Coagulation

Coagulation influences the number of CCN in the atmosphere active at a particular supersaturation in two key ways: (i) particle growth and mixing of constituents, affecting mixture hygroscopicity; and (ii) particle number loss. Coagulation is most efficient for particles of disparate size (e.g. small + large, where "small" and "large" should be viewed in relative, rather than absolute, terms).[88] The new particle diameter upon coagulation, assuming that both the colliding particles and the resulting particle are spherical, is:

$$d_{p,coag} = \left(\frac{6}{\pi} V_{p,coag}\right)^{\frac{1}{3}} = \left(\frac{6}{\pi}\left(V_{p,1} + V_{p,2}\right)\right)^{\frac{1}{3}} = \left(d_{p,1}^3 + d_{p,2}^3\right)^{\frac{1}{3}} \quad (16)$$

where $V_{p,x}$ is the spherical-particle volume for the coagulating (x = coag) and the two colliding particles (x = 1,2). If $d_{p,1}$ is large and $d_{p,2}$ is small, the overall increase in $d_{p,coag}$ relative to $d_{p,1}$

is nominal but substantial relative to $d_{p,2}$. For reference, in the case where two particles of equivalent diameter collide, the increase in (spherical) diameter is only a factor of 1.26. This increase in size corresponds to a decrease in s_{crit} relative to the initial particles, even for coagulation of particles of equivalent composition, but a halving of the total number concentration of potential CCN.

Coagulation also leads to changes in particle composition and is an important aging mechanism that serves to increase the degree of internal mixing of the atmospheric aerosol. Assuming that the volume mixing rule applies, and using the κ-Köhler formulation, the bulk hygroscopicity of the coagulated particle is:

$$\kappa_{coag} = \kappa_1 \cdot \epsilon_1 + \kappa_2 \cdot \epsilon_2 = \frac{\kappa_1 d_{p,1}^3 + \kappa_2 d_{p,2}^3}{d_{p,coag}3} \quad (17)$$

where spherical particles are assumed. Thus, coagulation of particles with different hygroscopicities leads to an increase in the resulting particle's hygroscopicity relative to the hygroscopicity of one of the initial particles, and a decrease relative to the other. Regardless of the final mixture hygroscopicity, the final particle always has a lower s_{crit} relative to either initial particle. This is illustrated in Figure 11 for the coagulation of 40 nm and 80 nm particles with varying hygroscopicity (κ = 0.01, 0.15 or 0.67). Coagulation of particles with the same hygroscopicity gives an indication of just the effect of increasing the particle size. The most substantial decreases in s_{crit} are found when a small, highly hygroscopic particle coagulates with a larger, less hygroscopic particle. However, most combinations lead to only a moderate decrease in s_{crit}. In other words, coagulation is relatively inefficient at making a population of particles more CCN active via changes in hygroscopicity or particle size distribution.

Coagulation can, however, have a substantial impact on the number concentration of particles with s_{crit} below some threshold value by decreasing the total number of particles in a given air mass. The particles with s_{crit} values less than the threshold value (e.g. 0.3% or 1%) can be considered potential CCN. Coagulation acts to scavenge potential CCN, whereas condensational growth will typically serve to increase the number of potential CCN in an air mass by decreasing the s_{crit} of the growing particles. The impact of coagulation on potential CCN concentrations in an air mass therefore depends on the relative rates of condensational growth versus coagulation. Coagulation rates depend on the particle number concentration, and thus are typically largest near sources of ultrafine (<100 nm) particles and decrease as air

masses are diluted into the background atmosphere. However, condensational growth rates are also typically largest near sources, and thus the exact competition between growth and particle number loss is dependent on the exact atmospheric conditions.[89]

4.4 Mixing state

Individual particles in the atmosphere show a diversity in their compositions that depends on proximity to sources, mixing of disparate air masses and the influence of secondary formation, among other processes. Measurements made using field-deployable single particle mass spectrometers[90] and from single particle microscopy (e.g. transmission electron microscopy[91] or scanning transmission x-ray microscopy[92]) indicate that particles with distinct properties can coexist within a given air mass.[93] Differences in composition between individual particles in a given air mass, or similarly the presence of different modes that might be comprised primarily of particles with distinct compositions, will lead to differences in the ability of these particles to activate into cloud droplets. The importance of mixing state, or at least of considering size-dependent variations in composition, is evident in some ambient observations of CCN number concentrations that assess the level of "closure" between observed and calculated CCN concentrations,[86a,94] in measurements of CCN associated with primary sea spray particle emission,[95] and in measurements of sub-saturated particle hygroscopicity often showing evidence of multiple particle types with distinct hygroscopicities.[96]

Air quality and climate models represent the mixing state of particles with varying levels of sophistication,[97] ranging from treating the particles as either completely externally or completely internally mixed with sectional or modal representations of different distributions[98] to semi-explicit treatment of the mixing state in a source-oriented approach[99] to having an explicit treatment of individual particles.[100] The fraction of particles that will be calculated to activate into CCN at a given s for a given particle size distribution is dependent upon the treatment of mixing state.[101] (Model predictions of CCN activity are also highly sensitive to the ability of models to accurately represent dry particle size distributions.[98]) The role that mixing state plays in determining the number of particles that are available as CCN at a given s is illustrated in Figure 12. Here, results are shown for a hypothetical bimodal size distribution and two component mixture with a low ($k = 0.07$) and high ($k = 0.67$) hygroscopicity component. Results are shown assuming that $s = 0.3\%$ or 1.0%. The overall distribution is assumed to be (i) completely internally mixed, (ii) completely externally mixed with no size

dependence, or (iii) completely externally mixed where the two modes are comprised entirely of the low or highly hygroscopic component. For this last case, it is either assumed that the low hygroscopicity component comprises the larger mode (iii-a) or the smaller mode (iii-b), meaning that the particles exhibit a size-dependent hygroscopicity. In general, the size-independent external mixture case leads to somewhat fewer particles activating into droplets compared to a complete internal mixture, with differences on the order of 10-20% (dependent upon *s*). Compared to the internal mixture, the size-dependent external mixture can lead to slightly more (iii-a) or substantially fewer (iii-b) particles that have critical supersaturations below the selected threshold. Case (iii-b) is consistent with an increase in hygroscopicity with particle size, and is closer to what is typically observed in the atmosphere. The particular influence of mixing state on the number of activated particles depends, of course, on the details of the size distribution and the maximum *s* achieved in a given cloud system, but the results shown in Figure 12 are reasonably general. They also illustrate the magnitudes of potential errors that can result when non-size-resolved composition measurements (e.g., $PM_{2.5}$ filter data) are used to reconstruct a CCN spectrum. Figure 12 only considers a binary distribution; real atmospheric particles will have distributions of hygroscopicities that vary with size that will further impact the general picture.

4.5 Timescales

The processes discussed above lead to modification of particle size distributions and composition on a variety of timescales. As we have described here, these changes are manifested as changes in the CCN spectra, the number distribution with respect to critical supersaturation. Many climate models account for such dynamical transformations in a simplified way, by converting essentially "non-CCN" particles ("hydrophobic") to "CCN-active" particles ("hydrophilic") using an exponential decay time constant,[8] typically of order of a day, although models are increasingly aiming to account for spatial and temporal variations in conversion timescales.[97,102] Of course, "CCN inactive" and "CCN active" are imprecise descriptions because the "CCN activity" must be referenced to a critical supersaturation. In the modeling context, "hydrophobic" may simply be used to refer to particles with critical supersaturations too large to activate in a particular cloud type, and the "hydrophobic-to-hydrophilic conversion" refers to the shift of critical supersaturation from above a threshold value for that cloud type, where the particle would be expected to remain as an interstitial particle, to below the threshold, where the particle can nucleate and grow into a cloud drop.

Assessment of appropriate ageing timescales is important in determining the lifetimes of atmospheric particles, which are generally controlled by precipitation scavenging and thus are linked to particle hygroscopicity.[103] For example, ageing timescales have been implicated as particularly important in determining the global distribution of black carbon-containing particles because of the strong impact of hygroscopicity on particulate scavenging.[104]

The importance of any one process (e.g. condensational growth versus coagulation) is determined by its timescale relative to the other processes and by the magnitude of the change that results from a given perturbation (for example, the magnitude of change in s_{crit} that results from a 1 nm change in diameter or a 1% change in κ).[105] In very general terms, the rates at which chemical and physical process transform particle size distributions and composition outside of cloud systems are fastest near sources (e.g. cities) where concentrations of particles, oxidants (OH, O_3, NO_3) and other chemical species (NO_x, SO_2, volatile organic compounds, etc.) are largest. Coagulation may be a particularly important near-source process for nighttime and early-morning emissions or in colder regions, when photochemical production of condensable material is slowed,[105] although this may be offset in regions where N_2O_5 concentrations are large. Further, coagulation rates are greatly slowed once total number concentrations are reduced to ~10^3 cm^{-3}. Daytime photochemical production of condensable material can lead to rapid growth of particles downwind of source regions, which serves to slow coagulation, add hygroscopic material, and grow particles. Simulations of "ageing" processes in an urban region suggest that coagulation and condensational growth can be highly competitive.[105] In contrast, although many studies have shown that heterogeneous reactions on particle surfaces occur and that they may alter hygroscopicity,[66] the reactions are often relatively slow and may only become important on longer (~1 week) timescales in the atmosphere, relative to the physical processes described above that rapidly act to transform the CCN spectrum.[69b] Scaling up of detailed model simulations to the global scale is challenging given the typical spatial resolution of climate models, but is nonetheless critical to understanding the global distribution and lifetimes of particles and their impacts on clouds.[106]

5 Summary

The ability of particles to serve as the nuclei for cloud drop formation depends on both their size and composition, which influence the particle's critical supersaturation. These two aspects cannot be separated, as size and composition are simultaneously affected by multiple chemical and physical processes that move particles through the diameter-critical supersaturation spaces

highlighted in Figure 4. The relative importance of a given chemical or physical process on CCN populations depends on the frequency of occurrence in the atmosphere, its rate relative to other processes that may modify or remove potential CCN, and on the impact of the process on particle number and critical supersaturation. Processes in which highly hygroscopic material is quickly added to particles (e.g., aqueous-phase chemistry) will have the most significant effect on the number concentrations of particles that will activate into CCN at a particular supersaturation, as both size and composition are affected in ways that decrease s_{crit}. Surface reactions and fragmentation processes have a comparably smaller influence on both size and hygroscopicity, and thus on critical supersaturation, although cannot be entirely neglected.

6 Suggested Future Research

Scientific understanding of the nature and abundance of particles capable of serving as CCN at typical cloud supersaturations has improved dramatically in the last few decades, due in large part to the advent of new, robust instrumentation for measuring activation spectra of ambient aerosols. However, there are several key chemical processes that require further study. These include the nature and role of surfactants in the atmosphere and their impact on surface tension; the morphology of CCN and the impact of non-sphericity on the application of Köhler theory and on CCN measurement and prediction; understanding how chemical processes impact the production of new CCN; and improved understanding of the timescales over which chemical and other processes change CCN properties, so that aging of the atmospheric aerosol can be properly represented in models of the aerosol life cycle.

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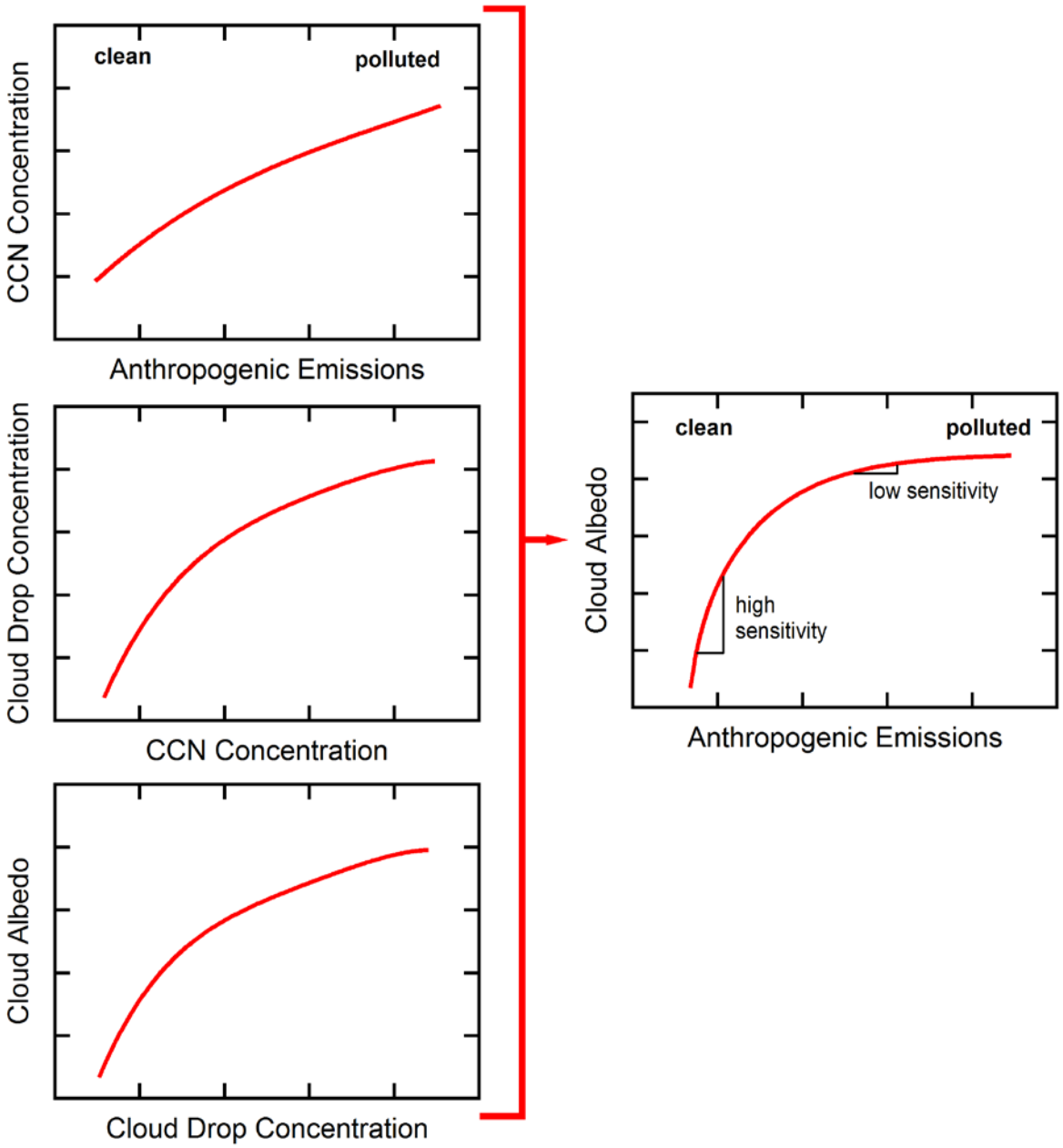

Figure 1. Illustration of the low, liquid cloud albedo climate effect, reflecting schematically typical relationships between (A) anthropogenic emissions and CCN concentrations, (B) cloud drop number concentrations and CCN concentrations, (C) cloud drop number concentrations and cloud albedo and, ultimately, (D) cloud albedo and anthropogenic emissions. Figure modeled after Carslaw et al.[8]

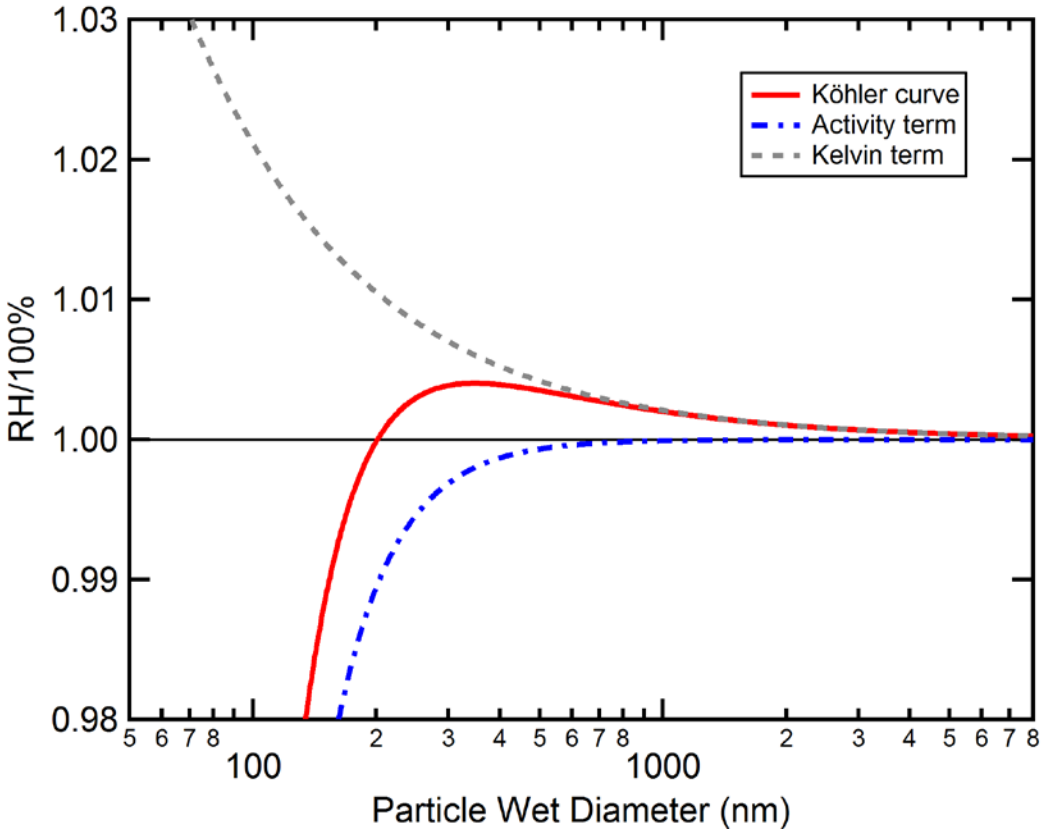

Figure 2. (A) Köhler curve (red line) for an ammonium sulfate particle with dry particle diameter = 50 nm, along with the related dependence of the Kelvin term (gray line) and water activity term (blue line) on the particle wet diameter. The vertical axis represents the vapor pressure over the particle, and is only equal to the ambient RH under conditions of equilibrium.

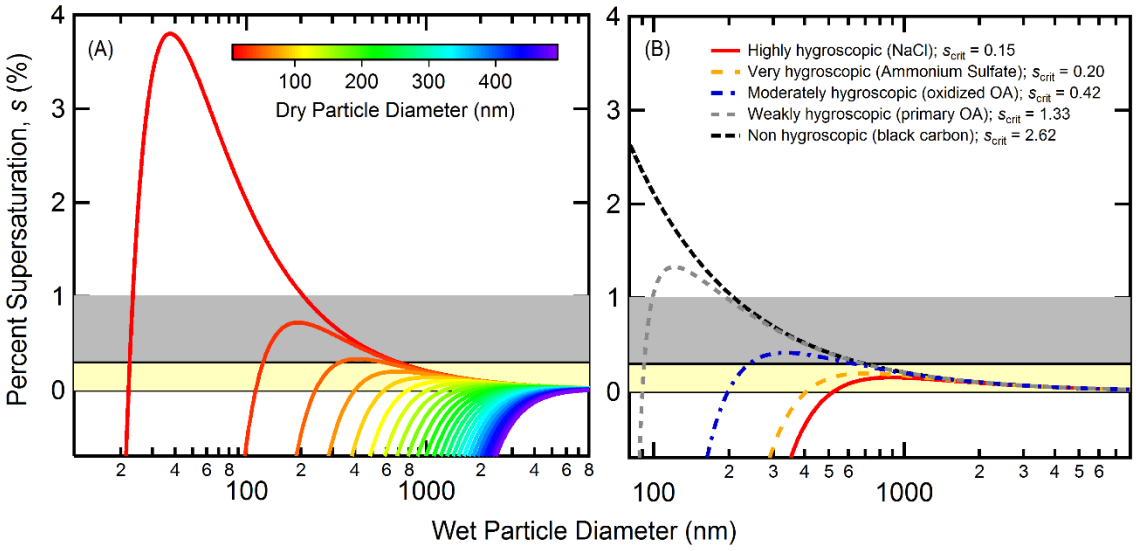

Figure 3. (A) Köhler curves for ammonium sulfate particles with dry particle diameters ranging from 10 nm to 490 nm, in 20 nm steps. The line color indicates the particle dry diameter. The gray filled region indicates where $s < 1.0\%$ and the yellow filled region where $s < 0.3\%$. Note the decrease in the critical supersaturation with increasing particle size. (B) Köhler curves for particles with 80 nm dry diameters but differing composition. Particles have been chosen to represent highly (NaCl), very (ammonium sulfate), moderately (oxidized organic aerosol), weakly (primary organic aerosol) and non- (black carbon) hygroscopic materials.

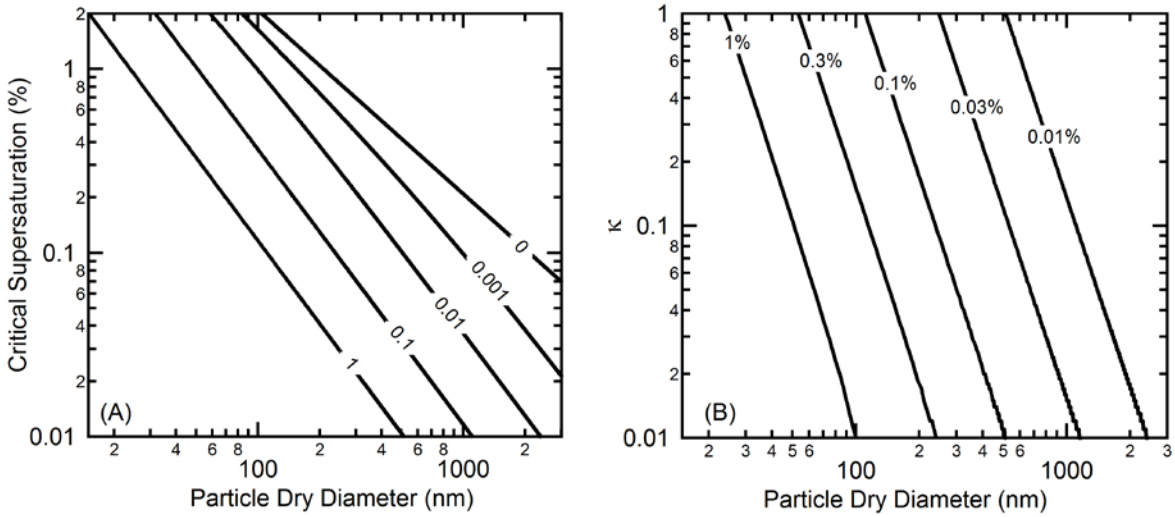

Figure 4. (A) The relationship between the critical supersaturation and dry particle diameter from 15 nm to 3 μm for particles of differing, but constant hygroscopicity. The lines correspond to values of the hygroscopicity parameter, κ, discussed in Section 2.2.1. Larger κ values indicate more hygroscopic materials. (B) The relationship between hygroscopicity (again, expressed as κ) and particle dry diameter for lines of constant s_{crit}.

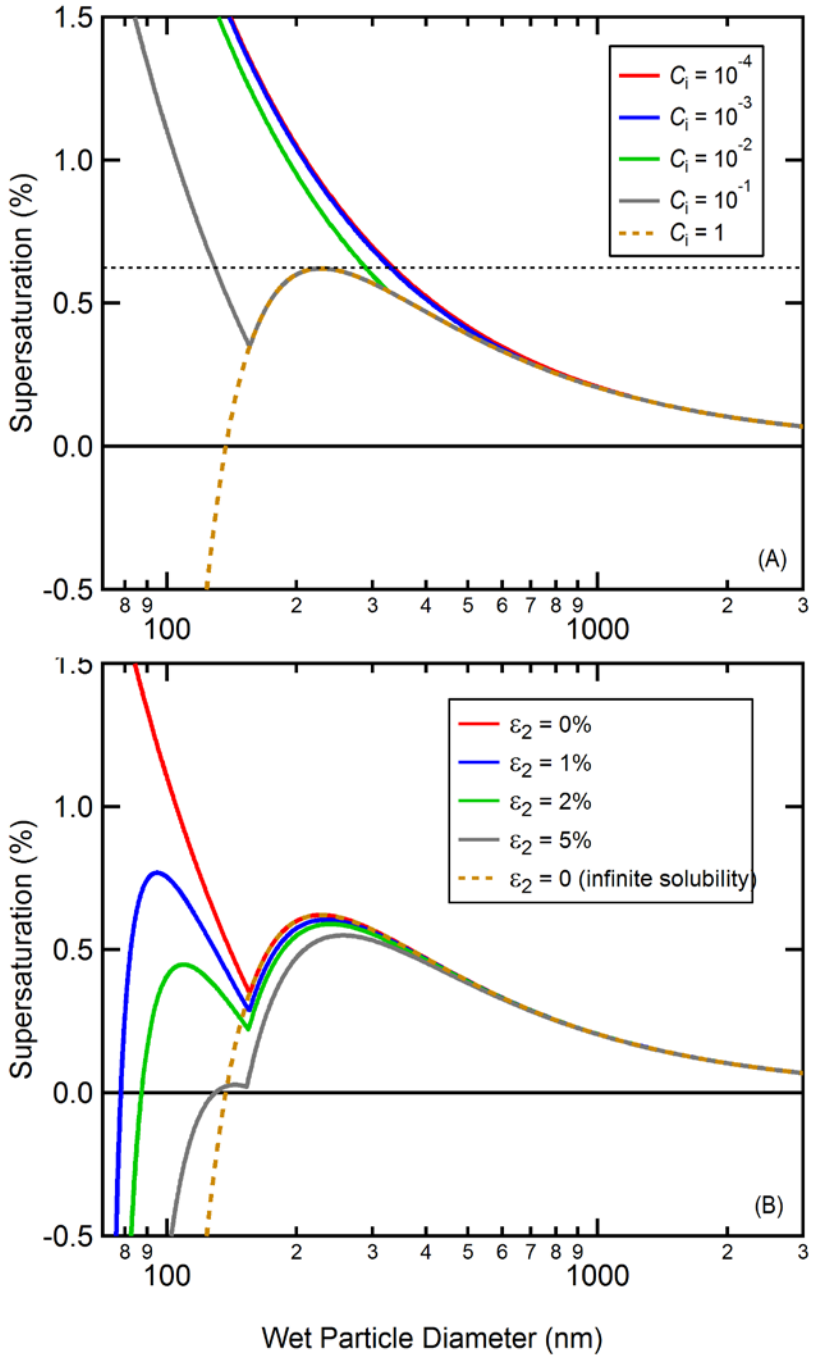

Figure 5. (A) Modified Köhler curves for partially soluble materials in a single component particle assuming $\kappa = 0.1$ and a dry particle size of 70 nm. The different curves correspond to different solubilities, ranging from $C_i = 10^{-4}$ to 1. The horizontal dashed line indicates the value of s_{crit} for an infinitely soluble compound with the same hygroscopicity. (B) Modified Köhler curves for a two-component particle where the volume fraction (ε_i) of the two components is varied. The solid lines assume that Component 1 has $\kappa = 0.1$ and $C_1 = 0.1$ and Component 2 has $\kappa = 0.67$ and $C_2 = 1$. The dashed line illustrates the Köhler curve when $\kappa = 0.1$ with no solubility limitation ($C_i = \infty$).

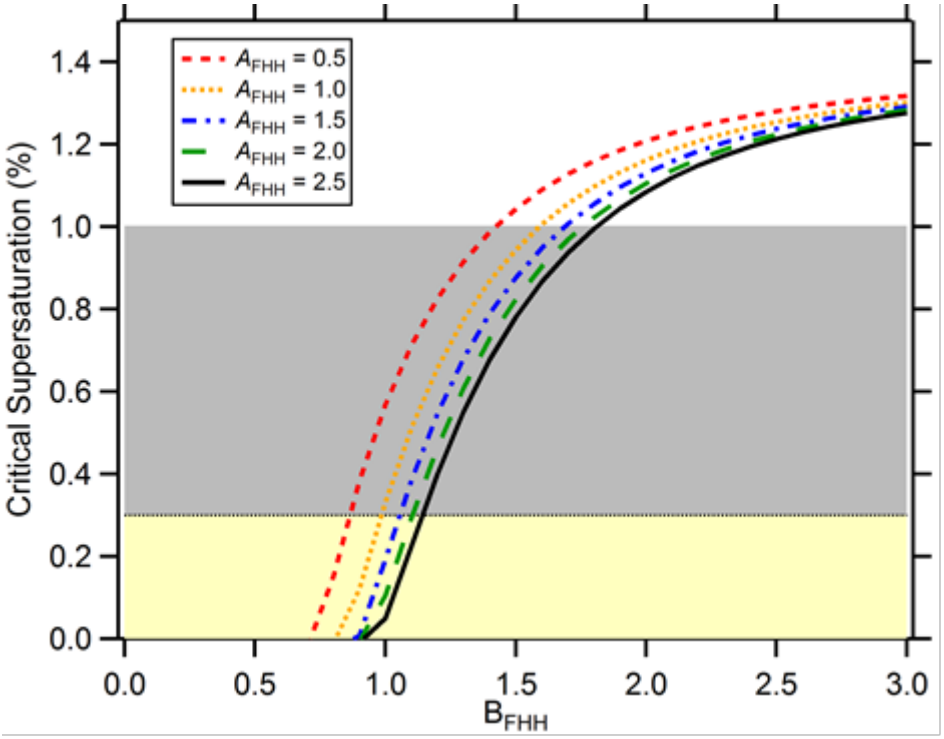

Figure 6. Variation in the critical supersaturation, s_{crit}, for a 150 nm particle that activates through adsorptive water uptake as a function of the parameter B_{FHH}, which is one of the parameters that describes the adsorption isotherm behavior. Adsorption curves are shown for different values of the other isotherm parameter, A_{FHH}. The yellow shaded region indicates where s < 0.3% and the gray shaded region where s < 1%. Recent lab studies suggest that appropriate parameters for representing aerosolized soil samples are A_{FHH} ~2.25 ±0.75 and B_{FHH} ~1.2 ±0.1.[35b]

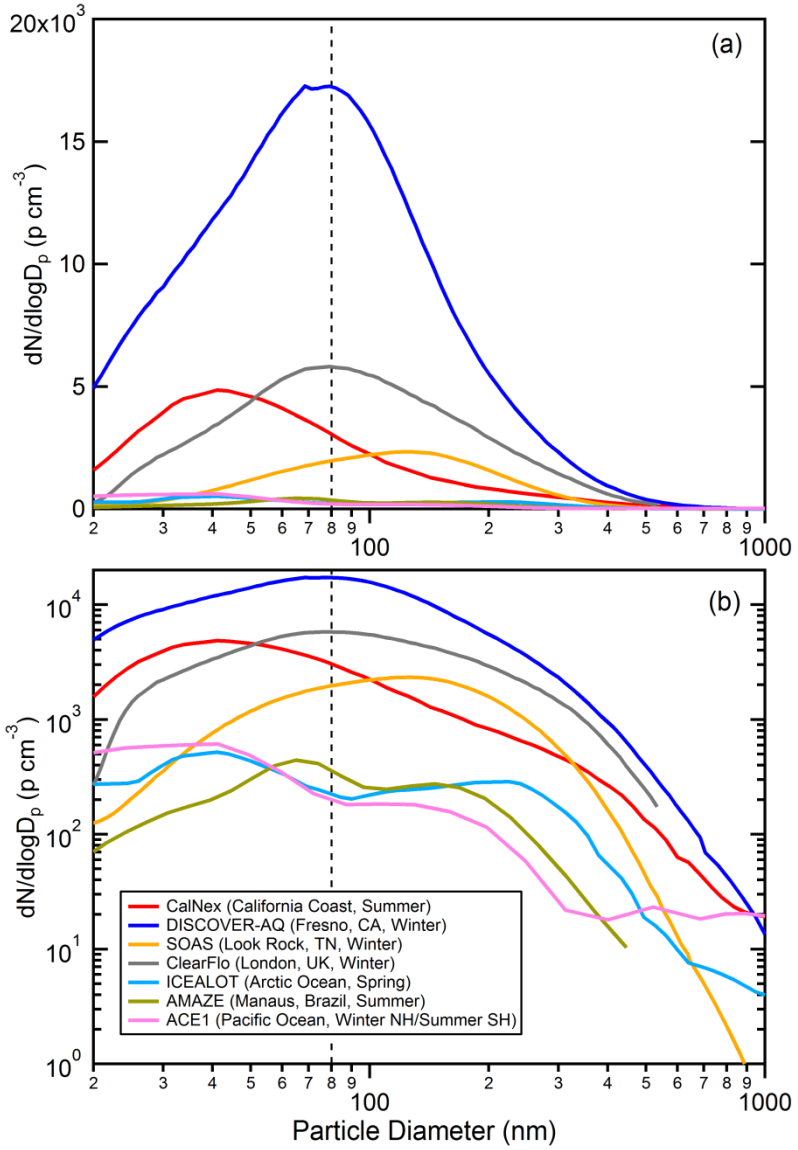

Figure 7. Example size distributions from surface-level measurements made around the world in (a) linear and (b) log scales for the y-axis. The vertical dashed line indicates a typical diameter used as a "CCN proxy" in analyzing the output of global aerosol models,[107] and refers to the dry particle diameter that corresponds to Scrit ~0.2% for kappa of ~0.5, values that may be typical in many stratus clouds." The legend gives the campaign name, location and season.

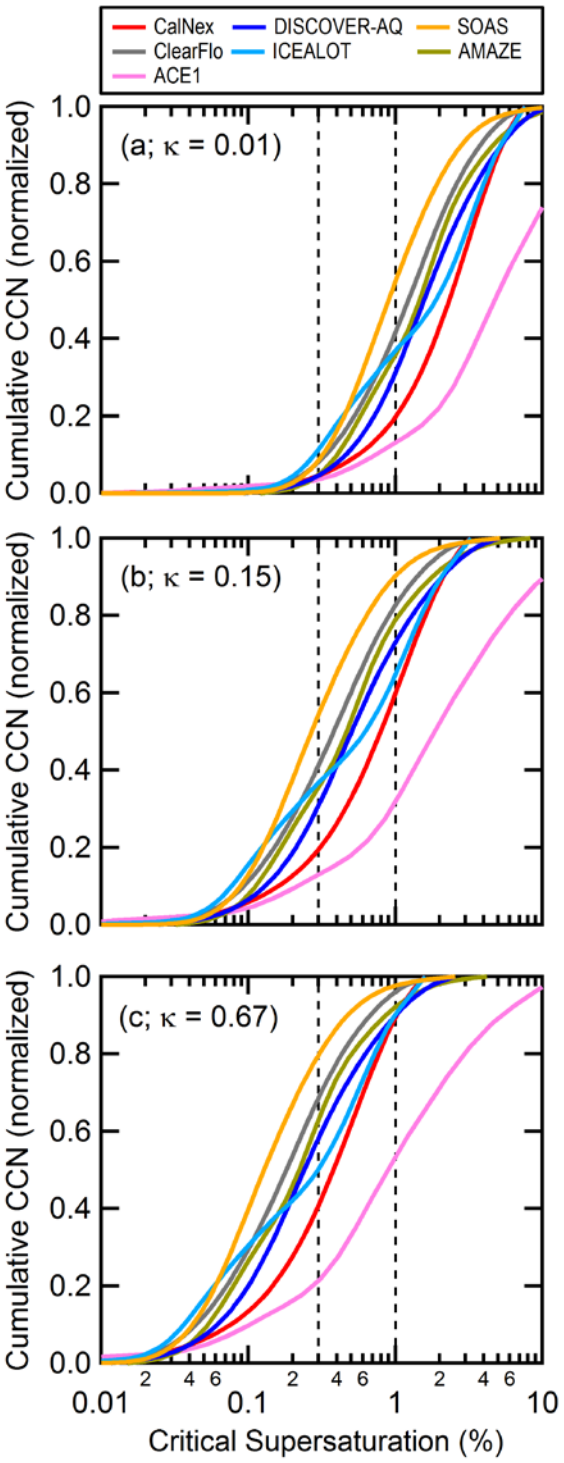

Figure 8. Cumulative number of CCN (normalized to total CN) as a function of s_{crit} for the size distributions shown for (a) κ = 0.01, (b) κ = 0.15 and (c) κ = 0.67. The vertical dashed lines highlight the differences between the various cumulative distributions at s = 0.3% and 1%.

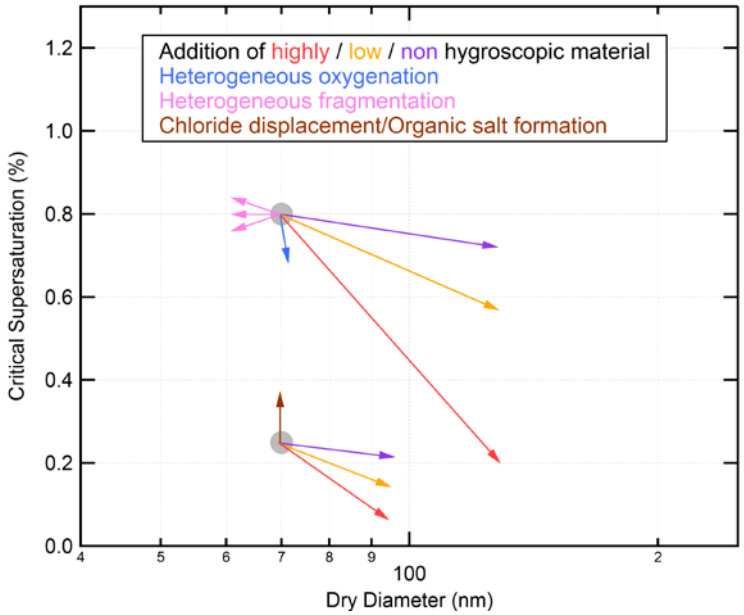

Figure 9. Atmospheric processes affect both the size and composition of particles, with consequent effects on the critical supersaturation required for activation. The general effects of common atmospheric processes (condensational growth, multiphase chemistry, chloride displacement, and heterogeneous oxidation, which is illustrated by fragmentation and oxygenation processes) are illustrated. The arrows indicate the impacts on particle dry diameter and critical supersaturation for each process for two example particles of the same size with different critical supersaturations. The arrow colors correspond to the processes indicated in the legend. The chloride displacement is more likely to occur for particles with lower s_{crit}, while heterogeneous organic oxidation chemistry is more likely to occur in organic-containing particles with higher $s_{crit.}$

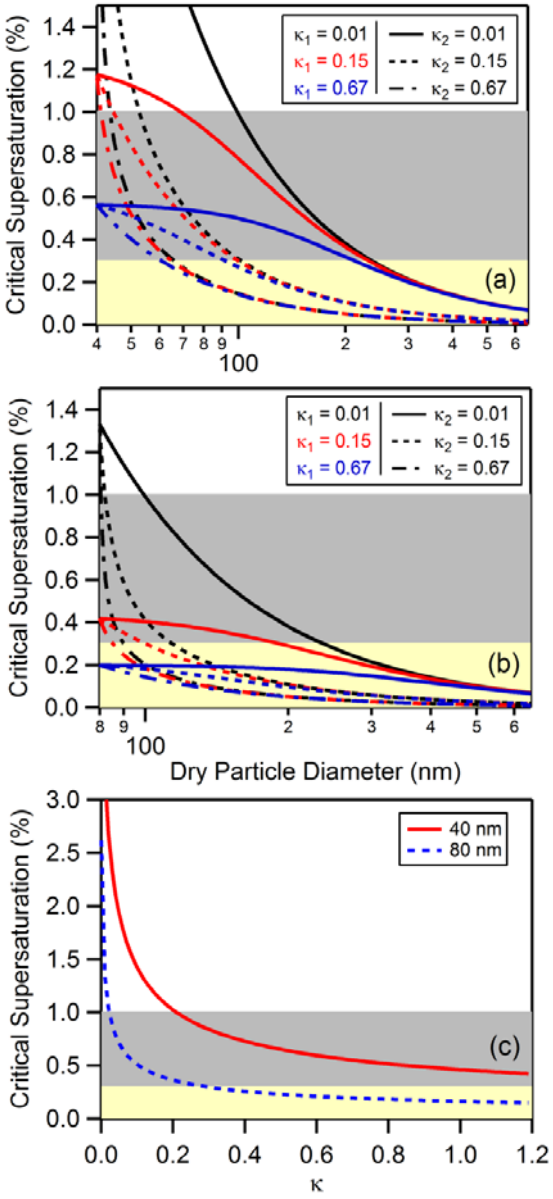

Figure 10. (a-b) Illustration of the influence of the addition of new material, or condensational growth, on the critical supersaturation of particles with different initial composition, as indicated by the different κ values of the starting material (κ_1) or added material (κ_2). Examples are shown for initial particles with dry diameters of (a) 40 nm or (b) 80 nm. The line colors indicate curves with the same starting material (black = κ_1 = 0.01; red = κ_1 = 0.15; blue = κ_1 = 0.67). The line styles indicate curves with the same condensing material (solid = κ_2 = 0.01; dashed = κ_2 = 0.15; dot-dashed = κ_2 = 0.67). The addition of even small amounts of a highly hygroscopic material, such as typical inorganic salts, leads to a rapid decrease in s_{crit} while the addition of material with lower hygroscopicity (κ = 0.15 and 0.01) leads to a more gradual decrease in s_{crit}, thus requiring growth to larger sizes to reach a given value of s_{crit}. (c) The critical supersaturation for particles of the indicated size, over the range of hygroscopicities indicated on the abscissa. The critical supersaturation exhibits a greater sensitivity to small changes in the hygroscopicity of low-hygroscopicity material (small κ). The gray and yellow bands in all panels indicate typical supersaturations (s = 1% or 0.3%, respectively) achieved in shallow cloud systems.

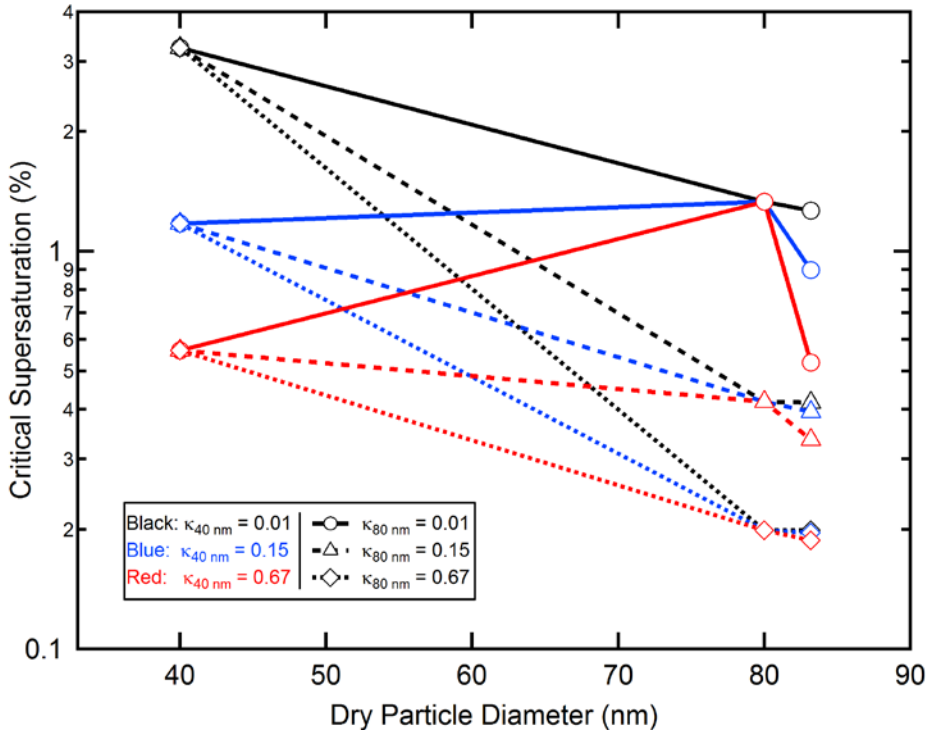

Figure 11. Illustration of the influence of coagulation on s_{crit}. Particles of $d_{p,dry}$ = 40 nm coagulate with particles of $d_{p,dry}$ = 80 nm to form a new particle with $d_{p,dry}$ = 83.2 nm. The initial particles have different hygroscopicities of κ = 0.01, 0.15 or 0.67, corresponding to low, moderate or highly hygroscopic particles. The s_{crit} of the initial particles and the resulting coagulated particle are shown, with pairs of particles connected by lines. The colors correspond to different κ values for the $d_{p,dry}$ = 40 nm particles (black = 0.01, blue = 0.15, red = 0.67), while the line/symbol styles correspond to the different κ values for the $d_{p,dry}$ = 80 nm particles (solid/circles = 0.01, dashed/triangles = 0.15, dotted/diamonds = 0.67).

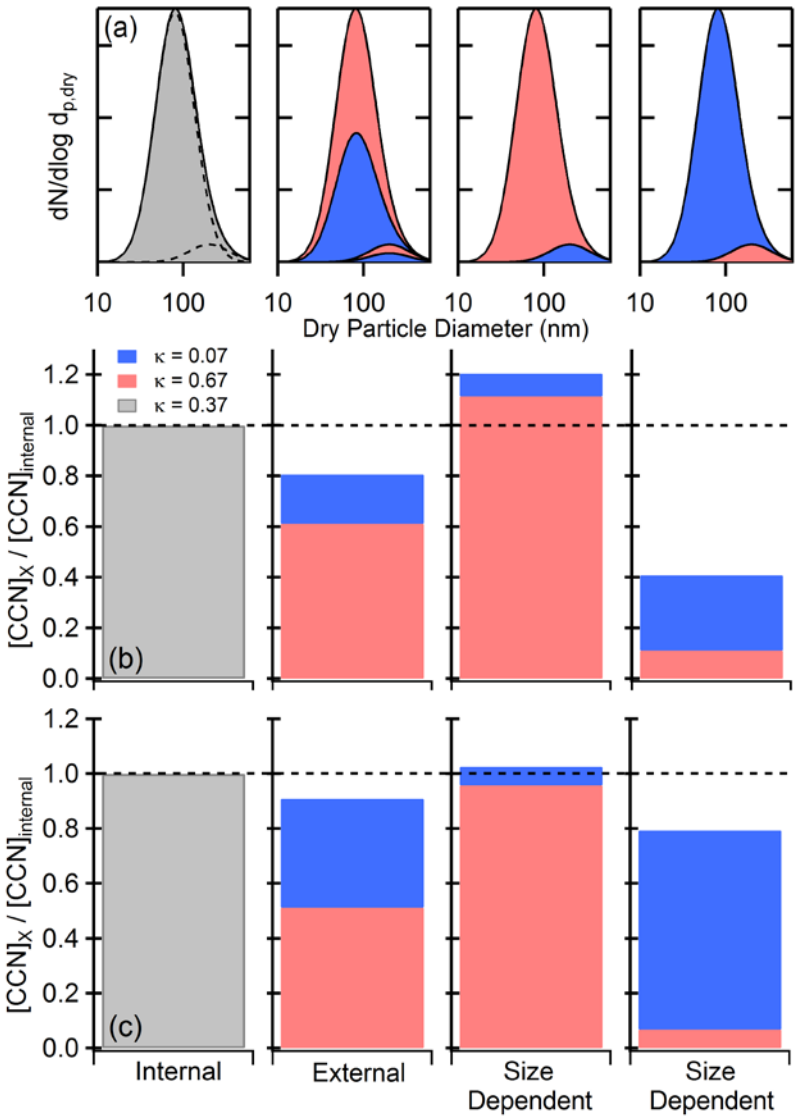

Figure 12. Illustration of the influence of particle mixing state on the number of particles that can be activated into droplets at a given *s*. Size distributions (a) and resulting CCN concentrations at 0.3% (b) and 1.0% (c) supersaturation, normalized to the internally mixed case, are shown for a hypothetical overall size distribution with two modes (median diameters of 80 nm and 200 nm, similar to the DISCOVER-AQ distribution in Figure 7) for a two component 1:1 by volume mixture. One of the components is assumed to have low hygroscopicity ($\kappa = 0.07$; blue colors) and the other high hygroscopicity ($\kappa = 0.67$; red colors). The internal mixture case assumes that all particles have equivalent compositions and the volume mixing rules apply (yielding $\kappa_{mix} = 0.37$). The external mixture assumes that the overall distribution is a mixture of two distinct particle types in equal concentrations. The size dependent case assumes that the two modes are comprised of particles with distinct hygroscopicities.