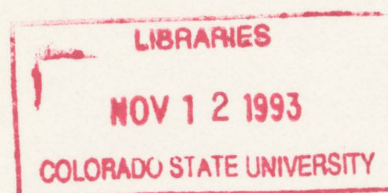


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A STUDY OF THE THEORETICAL BEHAVIOR OF
AMMONIUM SULFATE AEROSOLS IN THE
VICINITY OF CLOUD BASE

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A study of the theoretical behavior of Ammonium Sulfate Aerosols in the vicinity of cloud base

Bjorn Stevens

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Abstract

The theoretical behavior of hygroscopic aerosols in an environment typical of cloud base and sub-cloud regions is reviewed. Particular attention is paid to an evaluation of the appropriateness of a variety of assumptions typically made in the treatment of aerosol to cloud drop transitions. It is found that the ideal assumptions associated with the solute modification to surface vapor pressure involves significant errors for the small CCN. While small hygroscopic aerosols are well characterized by their equilibrium size, the slow response times of larger aerosols make them poor candidates for description by equilibrium theory. Non equilibrium effects are quantified as a function of size. The activation process is also considered for a variety of specified supersaturation fields. In general the activation of hygroscopic aerosols is not instantaneous, the lag time associated with activation is particularly important for the larger aerosols. The implications of these findings on numerical cloud models is discussed.

1 Introduction

The dynamic interaction of hygroscopic aerosols with their environment has been modeled in some detail since Howell's (1949) hand calculations of the growth of a distribution of cloud droplets existing in moist air cooled at a uniform rate. Another seminal paper on the interaction of aerosols with their environment is that of Mordy (1959) which brought Howell's calculations into the computer age and extended their considerations to study the effects of larger aerosols, varying updraft velocities, and differing aerosol number concentrations.

Subsequently aerosol studies have progressed and received financial support over time as they form a critical link in studies of visibility (Hänel, 1976), cloud precipitation efficiency and weather modification (Hobbs, Smith and Radke, 1980), or cloud radiative properties (Twomey, 1974, 1977). The last point is particularly relevant to current research as a change in the radiative properties of clouds can have significant climatic implications (Manabe and Wetherald 1967, Cess and others, 1984). It will be from this latter perspective that I examine the processes surrounding the transition of solution drops or haze particles to cloud drops.

In any attempt to numerically simulate the interactions of aerosols and cloud microstructure a correct simulation of the wet aerosol to cloud drop transition is critical. In this study I plan to address this issue in several steps. The first of which is presented here, where I will review in some detail the interactions between individual solution drops and an environment characteristic of the cloud base or sub-cloud regions of stratocumulus clouds. This study is conducted primarily from the perspective of the Ammonium Sulfate aerosol which is thought to dominate the activation process for marine stratocumulus clouds (Dinger and others, 1970). In particular I have identified (see Table 1) a set of five sample sizes



through which I will quantify many particular aspects of the mass dependent behavior of aerosols in an environment where the relative humidity approaches and exceeds saturation.

Table 1: Size table for sample set of five ammonium sulfate salts.

	CCN 1	CCN 2	CCN 3	CCN 4	CCN 5
Dry Mass (g)	4×10^{-18}	4×10^{-17}	4×10^{-16}	4×10^{-15}	4×10^{-14}
Dry Radius (cm)	8.14×10^{-7}	1.75×10^{-6}	3.78×10^{-6}	8.14×10^{-6}	1.75×10^{-5}

In subsequent parts of this study I hope to look at: (1) The interaction of a distribution of droplets with an evolving vapor field. (2) The effect on the activation process of random distributions of solution sizes for a specified solute mass, and small scale fluctuations in the supersaturation field on the droplet size. (3) Parameterizations of the activation process and their applicability for various modeling studies.

The outline of the remainder of this study is as follows: In Section 2 I review the behavior of hygroscopic aerosols in equilibrium with their environment, in particular I examine the validity of a number of assumptions commonly made in the equilibrium treatment of aerosols. Section 3 looks at details of aerosol growth toward equilibrium and activation under a variety of conditions. Section 4 is a summary in which the implications of the previous sections' conclusions on numerical cloud models is discussed.

2 Equilibrium considerations for hygroscopic aerosols

The equilibrium between multiple phases and constituents in a thermodynamic system is given by minimizing the internal energy, U , or maximizing the Entropy, S , of the heterogeneous system. Mathematically this can be expressed in term of the variation of the extensive variables:

$$(\delta S)_{U,V,n_k} \leq 0, \quad (\delta U)_{S,V,n_k} \geq 0$$

where V is the volume of the system and n_k is the amount of constituent k , both of which are kept constant during the variation.

In terms of the intensive variables this equilibrium condition requires that pressure, temperature and chemical potential remain constant across a surface of phase separation. These separate conditions are commonly referred to as mechanical, thermal and chemical equilibrium respectively. Thus for the system to be in thermodynamic equilibrium it must necessarily be in chemical, thermal and mechanical equilibrium, conditions of which require for a curved interface, two phase, two species system:

$$T'' = T' \quad (1)$$

$$p'' = p' + \frac{2\sigma}{r} \quad (2)$$

$$\mu_1'' = \mu_1' \quad (3)$$

$$\mu_2'' = \mu_2' \quad (4)$$

Where the superscript primes designate different phases and the subscript numerals denote the differing chemical constituents. The surface pressure, σ , modifies the pressure along the surface of a drop of radius r , and in general is a function of temperature and solute concentrations.

2.1 The generalized equilibrium relationship

A consideration of pressure balance yields Kelvin's equation for equilibrium between a drop in a vapor field, while equating chemical potentials across surfaces of phase separation yields the modifying effect of small concentrations of solute on the equilibrium vapor pressure over the drop. Considered together they yield the well known relation for equilibrium between an aqueous solution drop of radius r and humid air:

$$\frac{e_r}{e_s} = a_w \exp \left(\frac{2\sigma}{R_v T \rho_w r} \right). \quad (5)$$

Where e_r is the equilibrium vapor pressure over a drop of radius r , e_s is the saturation vapor pressure measured with respect to an infinite plane of pure water, a_w is the water activity of the solution drop, σ is the surface tension between the solution drop and the air, ρ_w liquid water density, R_v the gas constant for water vapor, and T is temperature in Kelvin. In the derivation of the above equation¹ all that was neglected was the enthalpy difference between the two phases and the specific volume of the liquid phase in comparison with the specific volume of the vapor phase. Both are excellent approximations.

2.2 Departures from ideality in the solute effect

In Equation (5) the presence of the factor a_w is a departure from most approaches which use the van't Hoff factor i and the ratio of the solute mass to the mass of water as an exponential modifier to the equilibrium vapor pressure over the drop. This results from only considering ideal solute interactions with the vapor field at the surface of the drop. Following Hänel (1976)² the correct formulation of the water activity for a solution drop can be constructed in terms of a number of empirical factors. Commonly the cloud physics literature speaks of the van't Hoff factor from which the following form of the water activity a_w follows,

$$a_w = \frac{n_w}{n_w + i n_s} = \left(1 + i \frac{M_w}{M_s} \cdot \frac{m_s}{m_w} \right)^{-1}, \quad (6)$$

where M is the molecular weight of solute (subscript s) or water (subscript w), m designates mass, and n designates mole number. Alternatively, physical chemists tend to prefer a description in terms of the practical osmotic coefficient, Φ_s :

$$a_w = \exp \left(-\nu \Phi_s \frac{M_w}{M_s} \cdot \frac{m_s}{m_w} \right), \quad (7)$$

with ν representing the number of ions a salt molecule dissociates into. The latter is a preferable description since values for it are more accessible (Robinson and Stokes, 1959) and it doesn't suffer from the ambiguity of definition which characterizes i , a point which we shall return to shortly.

For sufficiently dilute solutions Equation (6) above can be approximated:

$$\begin{aligned} a_w &= \frac{n_w}{n_w + i n_s} \approx 1 - i \frac{n_s}{n_w} \approx \exp \left(-i \frac{n_s}{n_w} \right) \\ &\approx \exp \left(-i \frac{M_w}{M_s} \cdot \frac{m_s}{m_w} \right). \end{aligned} \quad (8)$$

From a comparison of approximation in Equation (8) and the relation of Equation (7) one is tempted to form the equivalency $i = \nu \Phi_s$. This equivalency was used by Byers in his definition of a factor i_{Byers} which is often confused with the van't Hoff factor but is actually $\nu \Phi_s$ and only reduces to an equivalency with the van't Hoff factor for sufficiently dilute substances as discussed above (See Kunkel 1969, and Low

¹See Pruppacher and Klett chapter 4 - 6 for a much more detailed discussion of these points

²Also see Low, 1969a,b for original comments on this issue.

1969). Furthermore, for sufficiently dilute substances Φ_s approaches unity so that i approaches ν , and Equations (7) and (8) reduce to,

$$a_w \approx \exp \left(-\nu \frac{M_w}{M_s} \cdot \frac{m_s}{m_w} \right). \quad (9)$$

This then is the manner in which the solute effect on the equilibrium surface pressure over a solution drop is accounted for in many introductory texts. It offers the great advantage of having the modification of the vapor pressure over the drop depend logarithmically in direct proportion to the solute concentration, it is however not correct, as equating the van't Hoff factor i to the degree of dissociativity of the solute ν appears to have no physical basis, and is only done because for some species the numbers appear to be approximately equal.

In general, however, the modification of the equilibrium vapor pressure over a pure solution drop depends in a much more complicated manner on the relative concentration of the solute, and its chemical character. It is accurately described only in terms of the empirical relations given above and should as a matter of practice be described in terms of Equations (6) or (7) with i or Φ_s appropriately chosen. The extent to which the approximations bound up in Equation (9) are valid are measured by departures of Φ_s from unity. Φ_s is tabulated for our sample set of CCN under varying humidities in Table 2, and as is evident there, the assumptions of ideality (i.e., $\Phi_s = 1$) are far from being met. Another point which is evident in Pruppacher and Klett's (1978) Table 4-2 is that departures from ideality are much greater for Ammonium Sulfate than they are for either Sodium Chloride or Sodium Nitrate. The fact that Sodium Chloride tends to behave ideally may be a historical factor in the general neglect of these strong departures from ideality.

2.3 Relationship between solute mass, relative humidity and drop size.

Here I examine the effect of varying concentrations of solute on the radius r of a solution drop in equilibrium with its environment. One can consider the solute in terms of its effective volume radius a :

$$a \equiv \left[\frac{m_s}{\frac{4}{3}\pi\rho_s} \right]^{1/3},$$

so that a will be referred to as the radius of the dry aerosol; the assumption that the aerosol, when dry, takes the shape of a sphere is made implicitly. Since the mass of the water can be expressed in terms of drop radius and the aerosol radius, a : $m_w = \frac{4}{3}\pi\rho_w(r-a)^3$ for a given species, with water activity a_w described as per Equation (7); Equation (5) can be written:

$$\ln \left(\frac{e_r}{e_s} \right) = \frac{2\sigma}{R_v T \rho_w r} - \nu \Phi_s \left(\frac{\rho_s M_w}{\rho_w M_s} \right) \frac{1}{\left(\frac{r}{a} - 1 \right)^3}. \quad (10)$$

A condition of equilibrium is that vapor neither diffuse to or from the drop. This condition will be met only when the vapor pressure at the drop surface e_r , is identical to the ambient vapor pressure which I denote by e_∞ . Since $\frac{e_r}{e_\infty}$ is the relative humidity (RH), it is apparent by requiring the solution drop to be at equilibrium we force the left hand side of the above relation to equal the log of the relative humidity. For ease of notation we define the coefficients α , β , and γ ,

$$\alpha \equiv \frac{2\sigma}{R_v T \rho_l}, \quad \beta \equiv \nu \Phi_s \left(\frac{\rho_s M_w}{\rho_w M_s} \right), \quad \gamma \equiv \ln \left(\frac{e_a}{e_\infty} \right),$$

the form of Equation (10) can be further simplified:

$$\gamma = \frac{\alpha}{r} - \frac{\beta}{\left(\frac{r}{a} - 1 \right)^3}$$

$$= \frac{\alpha}{r} - \beta \left[\frac{a}{(r-a)} \right]^3, \quad (11)$$

where it should be recalled that the concentration and temperature dependence of σ and Φ_s are now implicit in the specification of the coefficients α and β . Thus, considering the parameters (α, β) to be constant, it is possible to solve for the equilibrium size r a dry hygroscopic salt of radius a will obtain at a given relative humidity. Equation (11) is just a reformulation of Köhler's equation, and solutions for a given a are known as Köhler curves.

Equation (11) allows for a general solution by multiplying it through by the factor $r(r-a)^3$ and collecting terms according to explicit dependence on r to some power. In so doing we construct a polynomial $f(r)$ for which $(a, \alpha, \beta, \gamma)$ are coefficients and whose zeros are solutions of (11). More specifically given that:

$$(r-a)^3 = r^3 - 3ar^2 + 3a^2r - a^3,$$

$f(r)$ follows by inspection,

$$f(r) = \gamma r^4 + (-3\gamma a - \alpha) r^3 + (3a(\gamma a + \alpha)) r^2 + (\beta a^3 - a^2(\gamma a + 3\alpha)) r + \alpha a^3 \quad (12)$$

where the polynomial reduces to third order for the case when the curvature and solute terms exactly cancel one another (i.e., $\gamma = 0$, RH = 100 %).

Solving the equilibrium relation by finding the zeros of the polynomial is most straight forward by assuming constant coefficients. To study the impact of the constant α and β assumptions I examined the case when β was reduced to 76.7 % of its original value. This was chosen as reflective of the effect departures from ideality would have on the solute term for molalities of 0.1 in Ammonium Sulfate; as is evident in Table 2, this is a reasonable departure from ideality. In Figure 1a the change in the solutions are less than the change in β , and for the RH = 95% curve, the influence of changes in β is relatively independent of solute mass. For the case of $\gamma = 0$, the sensitivity of the solution to the β term increases with increasing solute mass. However, as a increases concentration effects on β will diminish significantly (making our assumption of $\beta = 0.767\beta_{ideal}$ increasingly unrealistic, see for instance Table 2). For the sake of comparison I varied α similarly (i.e., decreased it to 76.7 % of its original value.) Differences due to variations of α quickly become negligible (see Figure 1b) in the RH = 95 % curve, while they mirror the changes in β seen in the $\gamma = 0$ curve. The latter is to be expected since for the $\gamma = 0$ polynomial α and β only enter into the 1st order term in ratio to one another.³

Thus a determination of whether the errors likely to be incurred for the assumption (β, α) independent of solution concentration (i.e., the ratio $\frac{\beta}{\alpha}$) depends largely on ones application; it is perhaps enough for our discussion to state that these assumptions have the potential to lead to significant although not overwhelming errors. Hereafter, and for purely pragmatic reasons, I will assume (α, β) independent of concentration effects as doing so allows me to examine other properties of equilibrium in a more straightforward manner.

In Figure 2 various curves are presented for ammonium sulfate and sodium chloride and their equilibrium sizes as a function of their dry size. These curves were obtained by solving for the zeros of $f(r)$ given in (12). These figures clearly show that equilibrium requires an extraordinary amount of growth for the largest aerosol salts as the relative humidity approaches 100%. As a result the largest aerosol rarely obtain their equilibrium sizes, a point we shall return to later.

A further assumption that is commonly made in conjunction with Equation (11) is that $a \ll r$ this greatly simplifies the solute term and allows for a simple analytic solution for the $\gamma = 0$ case:

$$r(\gamma = 0)_{r \gg a} = \sqrt{\frac{\beta a^3}{\alpha}}.$$

³This becomes apparent if you solve for the roots of the polynomial $f(r; \gamma = 0)/\alpha$.

Table 2: The 95, 99, and 100 % equilibrium sizes, concentrations (in terms of the Molality $\mathcal{M} = \frac{m_s/M_s}{m_w/1000}$) of solution at those sizes and the departure of solution drops from ideality for sample set of 5 CCN. Φ_s interpolated from water activity data tabulated in Low (1969a,b) via the relation: $\Phi_s = -\frac{1000}{M_w} \ln a_w$. Note, equilibrium sizes were calculated assuming ideality.

		CCN 1	CCN 2	CCN 3	CCN 4	CCN 5
$RH = 95\%$	Radius (cm)	2.40×10^{-6}	5.55×10^{-6}	1.24×10^{-5}	2.73×10^{-5}	5.94×10^{-5}
	$\mathcal{M}$	1.81	1.31	1.13	1.03	0.96
	Φ_s	0.6229	0.6297	0.6348	0.6387	0.6420
$RH = 99\%$	Radius (cm)	2.79×10^{-6}	7.07×10^{-6}	1.71×10^{-5}	3.93×10^{-5}	8.76×10^{-5}
	$\mathcal{M}$	0.94	0.48	0.31	0.24	0.21
	Φ_s	0.6430	0.6782	0.7048	0.7203	0.7299
$RH = 100\%$	Radius (cm)	3.00×10^{-6}	8.38×10^{-6}	2.41×10^{-5}	7.08×10^{-5}	2.12×10^{-4}
	$\mathcal{M}$	0.68	0.25	0.09	0.03	0.01
	Φ_s	0.6599	0.7176	0.7662	0.8888	≈ 1.0

As illustrated in Figure 3 this assumption leads to significant errors through out the range of aerosol sizes and relative humidities typically of interest to cloud physicists and so, in general, is unwarranted.

2.4 The Köhler Curves

Hitherto, I have examined the sensitivity of the equilibrium relations to a number of assumptions and outlined a procedure by which one can accurately calculate the equilibrium size at a given relative humidity. The classical method of describing equilibrium is via the Köhler curves which define a line in (r, γ) space for which solution drops of radius r are in equilibrium with the ambient vapor pressure described by γ (recall that $\gamma = \ln RH$). Several of these curves are plotted in Figure 4, each curve representing a differing mass of Ammonium Sulfate as per our sample set of 5 CCN. As these curves contain a wealth of information about the behavior of soluble salts in equilibrium with a vapor field they are well worth the extended discussion which follows. Furthermore, points raised subsequently are generalizable as curves for other soluble salts will differ only quantitatively from those plotted in Figure 4.

Broad characteristics The left hand side of the curves have positive slope and are entirely convex. In this region the curve traces a line of stable equilibrium in (r, γ) space. The right hand side of the curves have negative slope and are initially convex, but the second derivative quickly changes sign leading to concavity as the equilibrium line asymptotes toward $\gamma = 0$. The right hand side of the curve is well described by Kelvin's equation (see limiting dash-dot line) which implies that solution effects are negligible and equilibrium is described by a balance between drop radius and the magnitude of the ambient vapor field. In this region of (r, γ) space the curve traces out a line of equilibrium, but in contrast to the left hand side of the curve the equilibrium is not stable.

Stable equilibrium This property characterizes the equilibrium line on the Köhler curves' left hand side. It can be seen qualitatively by looking at the sketch given in Figure 5a. Here, a drop displaced from the equilibrium line to the left, will have an equilibrium vapor pressure given by $\gamma_{e,l}$ which is less

than the ambient vapor pressure given by γ_a . As a result the drop will act as a sink of vapor, causing vapor to diffuse to it from the environment, forcing growth which is represented by the dashed arrow as a movement toward the equilibrium line. Similarly for a drop displaced slightly to the right since $\gamma_{e,r} > \gamma_a$ vapor will diffuse from the drop to the environment, and the forcing will again be toward the equilibrium line as the drop shrinks.

Unstable equilibrium This situation behaves conversely to what was discussed above, here I refer the reader to Figure 5b. Because of the negative slope in this region of (r, γ) space a displacement of the drop to the left of the equilibrium line causes the equilibrium vapor pressure at the drops surface to rise, thus $\gamma_{l,e} > \gamma_a$ and the drop will continue to shrink, thereby displacing it even further from its equilibrium line. Likewise, a displacement to the right will decrease the vapor pressure at the drops surface thus causing vapor to diffuse toward the drop and as it grows it will be displaced increasingly further from the equilibrium line. This property of increased displacement from equilibrium after a slight perturbation is what characterizes this type of equilibrium as unstable.

Very stable/unstable equilibrium I have chosen to modify my equilibrium discussion with the use of the modifier *very* so as to distinguish regions of the curve where the slope of the equilibrium curve is steep vs. regions where it is relatively flat. A steep equilibrium curve implies that small excursions from equilibrium result in large differences between the ambient vapor pressure and the vapor pressure at the surface of the drop. The magnitude of the forcing on the drop will be proportional to this difference, so in regions of stable equilibrium a steep equilibrium curve implies that the drop will be strongly forced toward equilibrium, thus at low supersaturations or relative humidities the solution drops are strongly forced toward their equilibrium sizes, particularly for the smaller salts. This is the reason why smaller salts are commonly expected to exist at their equilibrium size. For the larger salts (see Figure 4) the equilibrium line becomes increasingly flat, which indicates that drops not in equilibrium with their environment are not strongly forced toward equilibrium (in the case of stable equilibrium). As a result larger aerosols rarely exist at their equilibrium size. In the unstable equilibrium part of the space we see that the curve is initially convex and becomes increasingly steep. This promotes rapid initial growth for newly activated drops as slight departures from equilibrium promote increasingly larger departures from equilibrium. This process continues for only a short period, however, as the equilibrium line quickly becomes concave and flattens out, thereby diminishing the vapor pressure forcing on the solution drop.

2.5 Aerosol activations

Droplet activation is a term used to designate the transition of the growth trajectory from a stable mode to an unstable one and is well described geometrically by the local maxima in the equilibrium curves in Figure 4. It can be found by solving for the radius at which the derivative of the equilibrium relation becomes zero. This radius is frequently designated as the activation radius or critical radius and is denoted by r_c . From Equation (11),

$$\frac{\partial \gamma}{\partial r} = -\frac{\alpha}{r^2} + 3\beta \left[\frac{a^3}{(r-a)^4} \right] = 0. \quad (13)$$

As before a polynomial, $g(r)$, can be constructed, for which the zero's represent solutions. So that r_c is defined implicitly such that $g(r_c) = 0$, where

$$g(r) = r^4 + (-4a)r^3 + (6a^2 - 3\beta a^3/\alpha)r^2 + (-4a^3)r + a^4 = 0. \quad (14)$$

Again using Equation (11), given r_c and solving for the equilibrium supersaturation γ_c :

$$\gamma_c \equiv \gamma(r_c) = \frac{\alpha}{r_c} - \beta \left[\frac{a}{(r_c - a)} \right]^3. \quad (15)$$

Which shows that the activation properties of soluble aerosols depend only upon the size and chemical composition of the aerosol (a, β), and the ambient temperature associated with α . The activation radius and supersaturations are plotted in Figure 2 (see solid lines) for Ammonium sulfate and Sodium Chloride. While specific values are tabulated in Table 3 for our sample set of CCN. This table demonstrates that the size range of aerosols chosen as our sample set clearly represent the size range of aerosols of interest to cloud physicists.

Table 3: Activation table for sample set of five ammonium sulfate salts.

	CCN 1	CCN 2	CCN 3	CCN 4	CCN 5
Activation Size (cm)	4.71×10^{-6}	1.35×10^{-5}	3.95×10^{-5}	1.18×10^{-4}	3.57×10^{-4}
Supersaturation (%)	1.74	0.594	0.199	0.066	0.021

The assumption $r \gg a$ discussed previously is most frequently made in conjunction with the activation properties of aerosols as doing so allows for a simple closed form description of activation properties of the aerosol:

$$r_c \approx r\left(\frac{d\gamma}{dr} = 0\right)_{r \gg a} = \sqrt{\frac{3\beta a^3}{\alpha}} \text{ and } \gamma_c \approx \sqrt{\frac{4\alpha^3}{27\beta a^3}}. \quad (16)$$

Unfortunately this approximation is not very accurate, particularly (see long dashed curves in Figure 3) for the smaller CCN which are well described by the equilibrium theory.

3 Diffusional Growth of Solution Drops

Equilibrium implies that the solution drop is in balance with the ambient vapor pressure. In other words the vapor pressure at the surface of the drop will be equal to that in the environment around the drop. Since diffusion is a down gradient process, this lack of a gradient in the vapor field between the drop and its environment will result in no net diffusion of vapor, and hence no further change in the mass of the solution drop. A drop not in equilibrium with its environment will be characterized by diffusional accretion (excretion) of water vapor to (from) its surface. As indicated qualitatively in the discussion of stable equilibrium of the previous section, larger soluble salts are more likely to be out of equilibrium with their environment as the forcing they experience toward equilibrium is relatively less than that experienced by a smaller mass of soluble material. Forcing toward equilibrium is just another way of speaking about the rate of droplet growth. To examine this issue more quantitatively requires an examination of the droplet growth equations.

3.1 Diffusional growth equations

In the presentation that follows I will be following the method outlined by Srivastava (1992) since it most elegantly presents the theory and its implicit approximations. My discussion deviates from Srivastava's in that ventilation effects are neglected while gas kinetic effects are accounted for. This is appropriate for small solution drops which will tend to be in dynamic equilibrium with their environment. The gas

kinetic effects are important for drops which have radii on the order of the mean free path of the air molecules. For drops which are on this order the assumption that the moist air is a continuous field right up to the drops surface breaks down. The break down in the diffusional theory can be mitigated by corrections to the parameters representing the diffusivity of water vapor and thermal conductivity of air. These "corrections" can lead to differences in D_v and k_a of many orders of magnitude for solution drops of sub-micron scale. To indicate corrections to the diffusivity and thermal conductivity parameters for gas kinetic effects, a superscript * is added to the standard variables. Using the definitions given by Pruppacher and Klett (1978):

$$\begin{aligned} D_v^* &= \frac{D_v}{\frac{r}{r+\Delta_v} + \frac{D_v}{r\alpha_c} \sqrt{\frac{2\pi}{R_v T}}} \\ k_a^* &= \frac{k_a}{\frac{r}{r+\Delta_T} + \frac{k_a}{r\alpha_T \rho c_p} \sqrt{\frac{2\pi}{R_v T}}} \end{aligned} \quad (17)$$

Where α_c and α_T are the condensation and thermal accommodation coefficients respectively; in the course of this study they will be taken to be constant⁴: $\alpha_c = 0.036$, $\alpha_T = 0.7$. Δ_T and Δ_v represent thermal and vapor jump lengths which denote the minimum distance from the surface of the drop for which the diffusion equation is valid; they too will be kept constant during the course of this study⁵: $\Delta_v = 1.04 \times 10^{-5} \text{ cm}$, $\Delta_T = 2.16 \times 10^{-5} \text{ cm}$. c_p is the specific heat of air at constant pressure and per unit mass, ρ is the density of the moist air, while R_v is the gas constant for water vapor.

For steady state diffusion of vapor the change in mass of the drop is described by the diffusion equation solved for a spherical system:

$$\frac{dm}{dt} = 4\pi r D_v^* (\rho_\infty - \rho_r), \quad (18)$$

where m is the mass of the solution drop, r is the radius of the solution drop (consistent with our previous discussion), D_v^* is the coefficient for the diffusion of water vapor corrected for gas kinetic effects, ρ_∞ is the ambient vapor density, and ρ_r is the equilibrium vapor density at the surface of the drop. Growth of the drop is additionally constrained by the ability of the environment to accommodate the heat liberated during the condensational process. Again assuming steady state processes and a spherical system one can form an equation for the diffusion of heat to the environment:

$$\frac{dQ}{dt} = 4\pi r k_a^* (T_r - T_\infty), \quad (19)$$

where Q is the amount of heat diffusing to or from the drop (depending on the relative magnitudes of the drop surface temperature T_r and the ambient temperature T_∞), and k_a^* is a measure of the thermal conductivity of air.

Neglecting radiation effects and processes other than the release of latent heat associated with the change in phase of vapor diffusing across the boundary of phase separation at the drops surface, the above equations can be related via,

$$L \frac{dm}{dt} = \frac{dQ}{dt},$$

where L is the latent heat of evaporation. From Equation (19) it is apparent that to solve for the change in mass of the droplet it is enough to solve for $\Delta T \equiv T_r - T_\infty$. Combining (18) and (19) with $\frac{dm}{dt} = \frac{1}{L} \frac{dQ}{dt}$

⁴See Pruppacher and Klett, 1978. Values taken from Table 13-1

⁵*ibid*

yields:

$$\Delta T = \frac{LD_v^*}{k_v^*}(\rho_\infty - \rho_r) \quad (20)$$

$$= \frac{LD_v^*}{k_v^*}[\rho_{s,\infty}(s_\infty + 1) - \rho_{s,r}(s_r + 1)], \quad (21)$$

where subscript s denotes the saturation vapor density which by Gibbs phase rule is a function of one thermodynamic variable only, which I take to be temperature. Furthermore, I denote the nature of the temperature dependence via the second subscript: $\rho_s(T_r) \equiv \rho_{s,r}$ and $\rho_s(T_\infty) \equiv \rho_{s,\infty}$. s_∞ is defined as the ambient supersaturation of the environment while the modification to the vapor pressure along the droplets surface is denoted by s_r :

$$s_\infty + 1 \equiv \frac{\rho_\infty}{\rho_{s,\infty}} = \frac{e_\infty}{e_s} \quad \text{and} \quad s_r + 1 \equiv \frac{\rho_r}{\rho_{s,\infty}} = \frac{e_r}{e_s} = e^\gamma,$$

where the last equality is based on the definition of γ from the previous discussion.

Even though the equation for ΔT depends implicitly on T_r a closed form solution may be constructed by using a Taylor series expansion for $\rho_{s,r}$ about T_∞ and truncating after the first order expansion. In general a linear fit to saturation vapor density is not a good approximation (Srivastava 1992), however in the case of condensational processes, $\Delta T/T_\infty \leq 10^{-5}$ (Neilburger and Chien, 1960) so for the purposes of our study the first order Taylor series expansion is a very good approximation. As a result Equation (21) simplifies:

$$\Delta T = \frac{LD_v^*}{k_v^*} [\rho_{s,\infty}(s_\infty + 1) - (\rho_{s,\infty} + \rho'_{s,\infty}\Delta T)(s_r + 1)], \quad (22)$$

where superscript prime represents differentiation with respect to the argument. Yielding upon rearrangement, an equation for ΔT entirely in terms of the ambient temperature⁶:

$$\Delta T = \frac{LD_v^*\rho_{s,\infty}(s_\infty - s_r)}{k_a^* + \rho'_{s,\infty}LD_v^*(s_r + 1)}. \quad (23)$$

Using (19) it is straight forward to solve for the change in the mass of the solution drop by substituting for ΔT from above:

$$\frac{dm}{dt} = 4\pi r \left[\frac{k_a^*D_v^*\rho_{s,\infty}(s_\infty - s_r)}{k_a^* + \rho'_{s,\infty}LD_v^*(s_r + 1)} \right]. \quad (24)$$

With $m = m_s + m_w$ (both of which were defined in the previous section),

$$\frac{dm}{dt} = \frac{dm_w}{dt} = 4\pi\rho_w(r - a)^2\frac{dr}{dt},$$

since the mass of the solute dissolved in the solution drop will remain invariant (i.e., $\frac{dm_s}{dt} = 0$). This then allows a formulation of the droplet growth equation in terms of radius:

$$\begin{aligned} \frac{dr}{dt} &= \frac{r}{\rho_w(r - a)^2} \left[\frac{k_a^*D_v^*\rho_{s,\infty}(s_\infty - s_r)}{k_a^* + \rho'_{s,\infty}LD_v^*(s_r + 1)} \right] \\ &= \frac{r}{\rho_w(r - a)^2} \left\{ \frac{s_\infty - s_r}{\frac{1}{D_v^*\rho_{s,\infty}} + (s_r + 1)\frac{L}{k_a^*}\left(\frac{\rho'_{s,\infty}}{\rho_{s,\infty}}\right)} \right\}. \end{aligned}$$

⁶This statement is true only if we implicitly take advantage of the near equality between T_r and T_∞ and replace the former with the latter—with little loss in accuracy—in the definition of α which appears implicitly in s_r via the definition of γ (see Equation (11)).

Via the ideal gas law the above equation finds expression in terms of saturation vapor pressure and its first derivative which can be solved using Clapeyron's equation,

$$\left(\frac{\rho'_{s,\infty}}{\rho_{s,\infty}}\right) = \frac{e'_{s,\infty}}{e_{s,\infty}} - \frac{1}{T} = \frac{L}{R_v T^2} - \frac{1}{T},$$

so that the droplet growth equation can be expressed in the more conventional form:

$$\frac{dr}{dt} = \frac{r}{\rho_w(r-a)^2} \left\{ \frac{s_\infty - s_r}{\frac{R_v T_\infty}{D_v^2 e_{s,\infty}} + (s_r + 1) \frac{L}{k_a T} \left(\frac{L}{R_v T_\infty} - 1 \right)} \right\}. \quad (25)$$

Further approximations generally involve neglecting s_r with respect to 1 and a with respect to r in the denominator. The former is generally a good assumption since in most situations of interest s_r will be on the order of 0.01 or less. The fact that the denominator size factor is given by $\frac{r}{(r-a)^2}$ as opposed to simply $\frac{1}{r}$ follows directly from the fact that the density of a solution drop is not constant and so when computing the relationship between mass and radius the change in density due to a change in solution concentration must be accounted for.

3.2 Numerical integrations of the droplet growth equation

In this section I conduct a brief study of the behavior of individual condensation nuclei in an idealized sub-cloud and cloud base layer. First I look at characteristic timescales at which solution drops approach equilibrium, this is then followed by an examination of the behavior of the set of CCN as they act as centers of vapor deposition and potentially activate in a supersaturated environment.

Calculations were based on solutions of Equation (25) with constants specified as per the discussion of the previous section. Solute and curvature effects were considered to act ideally (*i.e.*, (α, β) independent of concentration), although I chose⁷ $\Phi_s = 0.75$ for the ammonium sulfate solute and $\Phi_s = 0.93$ for calculations involving sodium chloride. Calculations for s_r were carried out at a temperature of 13°C, which is characteristic of stratus clouds observed during FIRE I (Schubert and others, 1987), and temperature modifications on the surface tension term were included as per Pruppacher and Klett (1978). Initial equilibrium sizes were calculated based on the polynomials of the previous section.

Before proceeding I verified my integration procedure for droplet growth with a comparison to values obtained analytically by Best⁸ (1951). The results are tabulated in Table (4). Best obtained his results via a graphical integration and did not account for gas kinetic effects or the changing density of the solution drop as it accumulates more liquid water mass. To account for discrepancies in growth times evident in Table (4) I repeated my numerical integrations with slight modifications to the growth equations. The results of these integrations are plotted in Figure (6), which are summarized below.

First I did a reference integration under the conditions associated with Table (4) where $m_s = 10^{-13}$ g and Sodium Chloride taken as the solute. I specified ambient temperature of 0 °C, an ambient supersaturation of 0.05%, and an initial solution drop radius of 0.75 μm . Φ_s was specified as indicated above. The results of this reference integration are those that are tabulated under the column Δt_{me} in Table 4. I then included a series of perturbations or modifying assumptions in the droplet growth equations:

⁷Except for the calculations associated with Figure 6, where $\Phi_s = 1.0$ was chosen to correspond to the calculations of the equilibrium radii of the previous section. As shown there, errors introduced by this assumption will be on the order of several percent.

⁸After being cited in Mason's book, and then again in the books on cloud physics by Rogers, and Rogers and Yau these calculations have attained the status of somewhat of a standard.

Table 4: The amount of time, Δt in seconds, it takes a sodium chloride solution drop to grow to the specified radius. Results from my integrations are compared with values obtained by Best (1951) for differing amounts of solute.

Radius (microns)	$m_s = 10^{-14}$		$m_s = 10^{-13}$		$m_s = 10^{-12}$	
	Δt_{Best}	Δt_{me}	Δt_{Best}	Δt_{me}	Δt_{Best}	Δt_{me}
1.0	2.4	4.61	0.15	0.146	0.013	0.003
2.0	130	248	7.0	7.66	0.61	0.286
5.0	1,000	1,370	320	343	62	41.6
10.0	2,700	2,910	1,800	1,670	870	190
15.0	5,200	4,770	4,200	3,470	2,900	1,650
20.0	8,500	7,050	7,400	5,710	5,900	3,700
30.0	17,500	12,900	16,000	11,520	14,500	9,280
50.0	44,500	30,100	43,500	28,570	41,500	26,000

Effect of Chemical Species: The long dashed-dot line in Figure (6) represents the solution to the growth equation for an amount of ammonium sulfate solute with dry radius equivalent to that for the control integration. The chemical species modifies growth only in terms of its effect on the solute term of the growth equation. This term is most important prior to activation, but for solute concentrations of the amount specified here initial radii of $0.75 \mu m$ already exceed the activation size. Barely discernable on the plot is the fact that the normalized drop size rapidly falls below unity, then maintains a rather steady normalized size at about 0.85, although after 30 minutes the ammonium sulfate solution drop has managed to gain to within about 91 % of the sodium chloride drop. Thus the effect of ammonium sulfate is to initially retard the drop growth, the fact that we are always at a normalized size of less than unity implies that the growth trajectory for ammonium sulfate is behind the trajectory for sodium chloride. The slow but steady approach to unity is consistent with the growth pattern of a slightly smaller drop for which solution effects are no longer important.

Constant density assumption: This normalized trajectory is represented by the long dashed (short space) line. The effect of assuming constant density is equivalent to saying that $r \approx (r - a)$ in the denominator of Equation (25). Here I show that this assumption only initially retards the growth of the solution drop. Since the initial radius size was relatively large, the effect of this assumption is relatively negligible and not likely to be a source of the discrepancy in the results of Table (4). Again the normalized radius slowly approaches unity, a reflection of the tendency toward monodispersity in the droplet growth equation.

Neglection of gas kinetic effects: For this integration I fixed $D_v = \lim_{r \rightarrow \infty} D_v^* = Const.$ I used a similar approach in obtaining constant values for the thermal diffusivity, k_v^* , but here instead of using the limiting values indicated in Pruppacher & Klett (1978), I used limiting values more representative of those chosen by Best. The results of this integration are more interesting (see the medium dashed line) and explain the differences between my results and those of Best as per Table (4). Initially the neglect of the gas kinetic effects give values for thermal diffusivities which are much too high, this makes the denominator in (25) too small, and thus the growth rate proportionally too large. Eventually the gas kinetic effects become negligible in the control integration and since we have a proportionally larger drop

its growth rate will be proportionally smaller suggesting an asymptotic approach toward a normalized radius of unity. Then, however, the effect of the different values for the diffusivity parameters becomes apparent as the solutions cross and continue to diverge, where after 30 minutes the drop has a normalized size of about 90 % of that of the control simulation. This crossing of the normalized trajectory over the unity line reflects initially more rapid growth followed by slower growth after gas kinetic effects become negligible. Thus the discrepancies between my time constants and those calculated by Best appear to be largely the result of the parameterization of the diffusivity parameters, with my integrations reflecting more current knowledge in our understanding of the behavior of these parameters.

Additionally Figure (6) illustrates the sensitivity of droplet growth to ambient temperature where the short dashed line represents the growth behavior of the control drop at 13°C. The enhancement of temperature increases the diffusion of vapor on to the drop allowing the drop to grow progressively larger, so that after 30 minutes of integration a drop growing at 13 °C is fifty percent larger than a drop growing at 0°C.

3.2.1 The forcing of individual solution drops toward equilibrium

Here I examine the time-scales under which solution drops move toward equilibrium under a variety of situations.

Table 5: The amount of time, τ in seconds, it takes a solution drop to grow from its 99 % to 100 % equilibrium size in the given supersaturation field for the sample set of 5 CCN. Also tabulated is $\chi_{i,j}$ which attempts to parameterize a relationship between dry CCN mass and time constants: $\frac{\tau_j}{\tau_i} = \left(\frac{m_j}{m_i}\right)^{\chi_{i,j}}$.

S (%)	τ_{CCN1}	τ_{CCN2}	τ_{CCN3}	τ_{CCN4}	τ_{CCN5}	$\chi_{1,2}$	$\chi_{1,5}$
2.0	0.0008	0.0056	0.0348	0.1881	0.9715	0.85	0.77
1.0	0.0013	0.0099	0.0623	0.3465	1.8367	0.88	0.79
0.5	0.0021	0.0164	0.1055	0.6110	3.3667	0.89	0.80
0.2	0.0036	0.0289	0.1915	1.1956	7.0730	0.90	0.82
0.1	0.0050	0.0415	0.2790	1.8660	11.8000	0.92	0.84

Characteristic timescales for the sample set of 5 CCN are tabulated in Table (5). This Table was constructed in an attempt to quantify the rate at which a solution drop will pass through various equilibrium sizes as it encounters higher supersaturations characteristic of the cloud base region. The range of timescales indicated for the sample set cover over 4 orders of magnitude and are roughly proportional to mass. The timescales are sensitive to the forcing (*i.e.*, an order of magnitude increase in the forcing results in a factor of 4 to 8 increase in τ) but the dominant factor is the amount of solute. As the mass of dry aerosols found in the troposphere span many orders of magnitude, the time constants for growth toward equilibrium will span many orders of magnitudes, from fractions of a second, to hours, or even days for the giant aerosols which I am not considering here.

In attempt to quantify this relationship between τ and dry mass m_d I define a parameter $\chi_{i,j}$:

$$\chi_{i,j} \equiv \frac{\ln(\tau_j/\tau_i)}{\ln(m_j/m_i)} \Rightarrow \tau_j = \tau_i \left(\frac{m_j}{m_i}\right)^{\chi_{i,j}}.$$

This parameter will give some quantitative measure of how the characteristic time at which a CCN approaches equilibrium varies as a function of mass and forcing. In particular I have tabulated $\chi_{i,j}$

derived from columns 1 and 5 as well as for columns 1 and 2. The fact that χ consistently increases for decreased forcing shows that the mass sensitivity of the characteristic times bears an inverse relationship to the forcing. Furthermore since $\chi_{1,2}$ is consistently greater than $\chi_{1,5}$ I conclude that the mass sensitivity factor χ bears an inverse relationship to mass in that it is largest when describing the sensitivity of τ to mass for the smaller CCN. Overall, however, it is apparent that the time constant as defined here bears a dependency on mass to some power where that power lies between 3/4 and unity.

These timescales are implicit in Figures (7) (a) and (b) where I have plotted the variation of the size of the sample set of CCN as a function of time in two different ambient relative humidities which are taken to be fixed. For both figures the initial size of the CCN was taken as its 95 % size. Plots of size are normalized to the equilibrium size for easier comparison between figures. (See Table 2 for these sizes). The time series of the different aerosols approaching their equilibrium size show the same order magnitude type relations to one another as seen in Table (5). These graphs display a number of features which are worthy of further discussion:

- (i) As was evident in Figure 2 the distance between the $RH_{95\%}$ and $RH_{99\%}$ equilibrium sizes vs. the distance between the $RH_{99\%}$ and $RH_{100\%}$ sizes is of the same order for the smaller CCN, but the latter becomes dominant with increasing solute mass. So while the $RH_{95\%}$ size of CCN5 is about 0.68 of its $RH_{99\%}$ size, it is only 0.28 of its $RH_{100\%}$ size. This should be contrasted with CCN1 whose $RH_{95\%}$ size is 0.88 of its $RH_{99\%}$ size, and 0.82 of its $RH_{100\%}$ size. Thus the larger CCN have proportionally a much greater distance to travel (in mass space) in their approach toward their $RH_{100\%}$ equilibrium size and most of this distance lies between their $RH_{99\%}$ and $RH_{100\%}$ sizes. Moreover, from Equation (25) the growth rate is inversely proportional to radius. In the figures the slopes look relatively equal, but accounting for the log scaling for time implies that visually equal slopes will differ drastically due to the increasing time scale along the abscissa. These effects in combination lead to the orders of magnitude increase in the time taken by increasingly larger CCN to approach their equilibrium size.
- (ii) As an illustrative example we see from the figures that CCN5 takes approximately 1 second to reach its $RH_{99\%}$ size, while it takes about 100 seconds to reach its $RH_{100\%}$ equilibrium size. Because of the orders of magnitude difference in time it takes to grow the largest of the CCN from its $RH_{95\%}$ size to its $RH_{99\%}$ size vs. the time it takes to grow to the $RH_{100\%}$ size it would seem that the assumption of a soluble aerosol being in equilibrium with its environment in the sub-cloud region becomes increasingly bad as the relative humidity of the subcloud region approaches 100 %.
- (iii) The growth rate of the CCN diminishes as it approaches its equilibrium size. In fact the approach to equilibrium is asymptotic as the numerator of Equation (25) approaches zero as the solution drop approaches its equilibrium size.

Other attempts have been made to measure the timescale at which solution drops approach equilibrium. Sedunov (1978) in assessing the validity of the assumption of equilibrium between condensation nuclei and their environment derives an expression for the characteristic time τ_s , for establishing equilibrium:

$$\frac{\tau}{\tau_{equil}} = 1 - (1 - r_0)e^{-\frac{t}{\tau_s}} \quad \text{where, } \tau_s \propto \frac{r_{equil}^2}{\gamma_{equil}}.$$

Since quantitatively Sedunov was measuring an e-folding time for drops approaching their equilibrium size from a small distance (in mass space) away, his actual numbers will differ considerably from ours.

However in terms of their proportional dependence on $r_{equil}^2 \propto m_{equil}^{\frac{2}{3}} \approx a^3 \propto m_s$ since the radius of the drop at activation is roughly a function of the radius of the solute to the power of three halves, they are

in general agreement with numbers I obtained earlier through numerical integration (i.e., $\chi_{Sedunov} \approx 1$). Sedunov's inverse dependence on γ_{equil} indicates that time constants for motion toward equilibrium depend on what the equilibrium is, and that as equilibrium approaches $RH = 100\% \Rightarrow \gamma_{equil} = 0$, τ can be expected to increase. Again, this feature of growth toward equilibrium is well represented in an intercomparison of Figure (7) (a) and (b).

Mordy in his celebrated 1959 paper also discusses a time constant, τ_m , associated with the e-folding time for a droplet forced toward equilibrium. In considering the approach to the 100 % equilibrium value Mordy argues that $\tau_m \propto m_s^{3/2}$. This represents a somewhat stronger dependence on the mass of the solute than what I found, however, Mordy's discussion was in the context of the $RH_{95\%}$ equilibrium size where the approach to equilibrium is slowest and most dependent on the mass of solute.

3.2.2 Numerical simulations of the activation process for individual drops in idealized supersaturation fields

In Figure (8) I have plotted a time series representing the evolution of the set of 5 CCN in constant supersaturation fields ranging from $s = 2\%$ to $s = 0.1\%$, with an ambient temperature of 13°C . These plots were constructed by integrating Equation (25) using a timestep of $2 \mu\text{s}$ and an initial radius for each category of CCN corresponding to its $RH = 95\%$ equilibrium size. In cooperation with Table 3 this figure provides an excellent illustration of the idealized activation process. It also illustrates that although activation is not an instantaneous process it can proceed very rapidly, as we have organized information with respect to time of activation for the different CCN in Table (6).

Table 6: Time τ in seconds for differing masses of solute to reach activation in the presence of a constantly supersaturated vapor field for drops initially at their $RH = 95\%$ size. * denotes no activation.

Supersaturation (%)	τ_{CCN1}	τ_{CCN2}	τ_{CCN3}	τ_{CCN4}	τ_{CCN5}
2.0	0.100	0.054	0.166	0.634	2.80
1.0	*	0.176	0.354	1.26	5.51
0.5	*	*	0.866	2.56	10.9
0.2	*	*	*	7.50	27.3
0.1	*	*	*	27.9	58.2

Of interest here is the general trend for the smaller CCN to activate before the larger CCN, despite the fact that the larger CCN will activate at a lower supersaturation. This is predominantly a result of the different growth trajectories associated with non-equilibrium effects. What is notable is that the smallest CCN (CCN1) takes proportionally much longer to activate than the next smallest (CCN2), a pattern of behavior which is inconsistent with our previous statement. While the steadily increasing activation times of CCN2 through CCN5 is a result of the increasing effect of non-equilibrium, the retarded activation rate of CCN1 relative to CCN2 is due to the fact that the ambient supersaturation for CCN1 is only slightly greater than that required for activation. As a result CCN1 is much more weakly forced toward its activation size. In terms of Equation (25) the retardation in the growth rate of CCN1 relative to CCN2 results predominantly from a reduction in the numerator term, while the progressive retardation in the activation time of CCN3 thru CCN5 relative to CCN2 is largely due to (1) the increased distance through mass space the larger CCN must travel to activate and (2) to their decreased growth rates due to a larger denominator in the growth equation.

This time series behavior plotted in Figure (8) brings out a number of interesting features which are itemized below:

- (i) Growth is most dramatic for the drops forming on the smallest mass of soluble aerosol. Furthermore the actual point of activation is clearly represented for the smallest CCN, but becomes increasingly difficult to discern for the larger CCN.
- (ii) With regard to Table (6) and our previous discussion it is clear that the tabulated activation behavior is well represented in the time series data.
- (iii) The effect of the surface tension in inhibiting activation is clear for the smallest aerosol as CCN1 doesn't activate in situations represented by Figure (8) (b)-(e), this is consistent with earlier conclusions that $s_{c,ccn1} \approx 1.8\%$ (see Table 3). In situations where CCN don't activate the movement of the CCN toward an equilibrium size and the maintenance of that size is represented in the plots, although it is difficult to see (look for instance at CCN3 in the last frame).
- (iv) Activation is most clearly represented by a convergence of the growth trajectories associated with the varying sized CCN. This behavior is well represented in all the plots

An interesting manifestation of the fact that the large CCN activate last in the above situation is that for very large CCN we may infer that they never activate, but continue to grow so long as $RH > 100\%$. This arises from the realization that the amount of time it takes the largest aerosols to grow to their activation size may conceivably be longer than their lifetime in the cloud.

This then raises some interesting questions: (1) To what extent can finite growth periods associated with all CCN influence whether or not a CCN will activate at all, particularly in cloud like situations where the maximum supersaturations may exist only for a short period of time. (2) Is it possible that in a rapidly varying supersaturation field that growth trajectories as plotted in Figure (8) could actually cross. In an attempt to address these questions I looked at the evolution of CCN in a more realistic supersaturation field which varies with time. In particular I chose a supersaturation field which approaches a maximum value of 1 % from an initial value of $RH = 95\% \Rightarrow s = -5\%$ and then decays to a final value of 0.1 %. The time constant for approach to the maximum value was five minutes, while the time constant for decay to the final value was increased to model differing scenarios under which solution drops would spend more or less time at or near the maximum supersaturation. Additionally the timestep for the numerical integrations was increased by a factor of 1000 to 2 ms, but otherwise the calculations are the same. The growth trajectories are plotted in Figure (9) along with the supersaturation fields. The time it takes for the varying sized CCN to activate is given in Table (7).

Table 7: Time τ in seconds for differing masses of solute to reach activation in the presence of a time varying vapor field (with $s_{max} = 1\%$, for comparison see row two of the previous table) for drops initially at their $RH = 95\%$ size. * denotes no activation.

Profile	τ_{CCN1}	τ_{CCN2}	τ_{CCN3}	τ_{CCN4}	τ_{CCN5}
1.0	*	87.7	64.4	63.2	72.4

While the supersaturation fields were chosen to be similar of those found in clouds it is not correct to conclude that the trajectories plotted in Figure (9) are necessarily representative of what one would expect to find in a real cloud, as the latter differs in at least two important and perhaps critical respects:

(1) Clouds are characterized by the growth of large populations of CCN. (2) The vapor deposited on these CCN interact strongly with the ambient vapor field. Nevertheless, my hope is that the behavior of CCN illustrated in the trajectories of Figure (9) are instructive and can contribute to a better understanding of the behavior of soluble aerosol salts in a supersaturated environment.

Table (7) has only one row since the activation time is the same regardless of the decay constant of the supersaturation field. This implies that the response time of the aerosols is rapid enough for the aerosols to reach their activation radius before the supersaturation begins to decrease. In Figure (9) the maximum supersaturation occurs at about the 130 second mark, while the last aerosol to activate does so at 87.7 seconds. Table (7) and Figure (9) bring out a number of additional interesting points which are itemized below.

- (i) The balance between stronger forcing (for the larger aerosols) and most rapid response (for the smaller aerosol's) favors CCN4 for most rapid activation. The supersaturation never gets large enough to cause CCN1 to activate, and CCN2 activates last due to the fact that the supersaturation does not reach the critical value for activation of CCN2 until about this time. While the supersaturation reaches the critical value for activation of CCN5 first, it is slower to activate due to its slow response time.
- (ii) Activation is most dramatic for the smaller CCN as after activation they rapidly grow to a size limited by the next larger CCN. This type of behavior demonstrates the tendency of a drops spectra to narrow under the influence of condensational growth. Growth trajectories show no signs, however, of crossing. Growth trajectories do not cross and show no inclination of that possibility. In order for growth trajectories to cross the reduction of vapor pressure over one drop must be greater than the reduction of vapor pressure over another drop of equal size but greater solute mass. However, for drops of equal size the drop with greater mass of solute (assuming same chemical composition) will always have the greatest reduction in vapor pressure and hence the greatest growth rate. Thus a crossing of trajectories is physically impossible a result with which any parameterization of the activation process must be consistent.
- (iii) The growth trajectories are plotted on a linear abscissa (Figure (10)), since linear time is a quantity more familiar to us. The dramatic activation process is still clearly evident and none of the main features described above.
- (iv) The growth of CCN1 to its non-activated equilibrium size is characterized by strong oscillations over the first 20 seconds. This feature was created intentionally to illustrate the problem of attempting to resolve the growth trajectories of small aerosols in numerical cloud models. The oscillations are not evident in Figure (8) since the growth equation was integrated for this figure with a time-step of 2 μ s. The fact that even a 2 ms timestep (which was used to create Figures (9) and (10)) is not sufficient to resolve the growth of the smaller aerosols, should be considered in the context of numerical cloud models which typically use timesteps on the order of seconds or tens of seconds.

4 Summary

It was found that for Ammonium Sulfate departures from ideality in the solute term were significant. With the practical osmotic coefficient commonly differing by 20 % from its ideal value. Nevertheless, predictions of equilibrium sizes resulting from a neglect of this effect tended to only be on the order of 5 - 10 % in error. Given the range of uncertainties in cloud modeling and aerosol measurements this is not an important source of error, but still it should be accounted for when possible, especially in theoretical studies or 1-D models.

Distances in mass space between equilibrium sizes were small for small amounts of solute, but tended to grow increasingly large for the larger sized CCN. Thus, the difference between the $RH_{99\%}$ and $RH_{100\%}$ sizes was proportionally much greater for the large aerosols. This is a major factor in making non-equilibrium effects important for the larger aerosols typically of interest. The quality of the equilibrium solution for solution drop sizes in a saturated environment is such that above a critical size equilibrium becomes unstable. The transition region between unstable and stable equilibrium represents a demarcation line between cloud drops and haze particles and represents a critical point for cloud modelers who are often interested in the dynamics of cloud drops but are not able to treat the behavior of the proto-drops or haze particles in a realistic manner. It is seen that common assumptions which neglect the radius of the solute in comparison to the drop when calculating equilibrium or activation sizes involves significant errors. Cloud models which have a means by which to measure CCN size before the activation process should use this size in determining the correct activation size of the CCN. Characteristic times at which CCN approach their equilibrium sizes differ in rough proportion to their mass. As atmospheric aerosols of interest in the formation of cloud often span four or more orders of magnitudes their growth rates will also widely differ. This presents a vexing problem for cloud modeler, since to resolve the growth of the smallest solution drops requires timesteps on the order of milliseconds. An alternative approach would be to diagnose the size of the smallest aerosols based on the rather good assumption that they are in equilibrium with their environment. Furthermore, this assumption should not significantly alter the structure of the vapor field since the smallest aerosols, despite their number, are unlikely to act as a large enough sink for water vapor to significantly interact with the vapor field in the cloud base region. As the aerosols increase in size however, they can interact more strongly with the vapor field (since they take up more water) but the assumption of them being in equilibrium will become increasingly bad. It would then seem that the vapor depositional processes of the larger aerosols should be calculated in a predictive manner if possible, or parameterized if not.

In contrasting the activation process for small and large Ammonium Sulfate CCN it was found that the activation process is most dramatic for the smallest CCN which activate first (given high enough supersaturations) in an evolving supersaturation field. The largest CCN can grow to the Hocking limit and never technically activate, being forced the whole time in a regime of stable equilibrium growth, as opposed to the activated cloud drops which grow in a regime which is characterized as unstable equilibrium. This illustrates an important property of the larger CCN as they may spend their entire (pre-collision) life in the cloud existing as solution drops or oversized Haze particles. In increasing supersaturation fields typical of cloud base, the medium sized aerosols will activate first. If supersaturations continue to increase smaller aerosols will activate subsequently, while larger aerosols will continue to activate, after a slight delay, even in a non-changing or slightly decreasing supersaturation field.

It is not possible for a given size solute to form a solution drop or cloud drop which is larger than that which will form on a larger amount of solute experiencing the same conditions. While activation becomes a relaxed property for the larger masses of solute this should not mislead one into thinking that the growth trajectories of a small mass of solute can ever cross those of a larger mass of solute. This could provide a valuable constraint for parameterizations of the growth of solution drops, as the condensational growth of the smallest aerosols will ultimately be limited by the growth of the largest aerosols.

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References

- [1] Best, A. C., 1951: The size of droplets in a layer-type cloud. *Quart. J. Roy. Meteor. Soc.*, **77**, 241.
- [2] Cess, R. D., G. L. Potter, J. P. Blanchet, G. J. Boer, S. J. Ghan, J. T. Kiehl, H. Le Treut, Z.-X. Li, X.-Z. Liang, J. F. B. Mitchell, J.-J. Morcrette, D. A. Randall, M. R. Riches, E. Roeckner, U. Schlese, A. Slingo, K. E. Taylor, W. M. Washington, R. T. Wetherald, I. Yagai, 1989a: Interpretation of cloud-climate feedback as produced by 14 atmospheric general circulation models. *Science*, **245**, 513-516.
- [3] Dinger, J., Howell, H. B., and Wojciechowski, 1970: On the source and composition of cloud nuclei in a subsident air mass over the North Atlantic *J. Atmos. Sci.* **27**, 1791.
- [4] Hänel, Gottfried, 1976: The properties of atmospheric aerosol particles as functions of the relative humidity at thermodynamic equilibrium with the surrounding moist air. *Advances in Geophysics*, **19**, 73-188.
- [5] Hobbs, P.V., J.L. Smith, L.F. Radke, 1980: Cloud-active nuclei from coal-fired electric power plants and their interactions with clouds. *J. Appl. Meteorol.*, **19**, 459.
- [6] Howell, W.E., 1949: The growth of cloud drops in uniformly cooled air. *J. Meteorol.*, **6**, 134-149.
- [7] Kunkel, Bruce A., 1969: Comments on "A generalized Equation for the solution effect in droplet growth." *J. Atmos. Sci.*, **26**, 1344-1346.
- [8] Low, R. D. H., 1969a: A theoretical study of nineteen condensation nuclei. *J. Rech. Atmos.*, **4**, 65-78.
- [9] Low, R. D. H., 1969b: A generalized Equation for the solution Effect in Droplet Growth. *J. Atmos. Sci.*, **26**, 608-611.
- [10] Mordy, W. A., 1959: computations of the growth by condensation of a population of cloud droplets. *Tellus*, **9**, 16-44.
- [11] Manabe, Syukuro and Richard T. Wetherald, 1967: Thermal equilibrium of the atmosphere with a given equilibrium of relative humidity. *J. Atmos. Sci.*, **24**, 241-259.
- [12] Neilburger, M., and C. W. Chien, 1960: Computations of the growth of cloud drops by condensation using an electronic digital computer. *Geophys. Monogr., am. Geophys. Union*, No. **5**., 191-208.
- [13] Pruppacher, Hans R., and James D. Klett, 1978: "Microphysics of Clouds and Precipitation." D. Reidel, Dordrecht Holland.
- [14] Robinson, R. A., and Stokes, R. H., 1959: "Electrolyte Solutions." Butterworth, London.
- [15] Schubert, W. H., Paul E. Ciesielski, Thomas B. McKee, John D. Kleist, Stephen K. Cox, Christopher M. Johnson-Pasqua, and William L. Smith Jr, 1987: Analysis of boundary layer sounding data from the fire marine stratocumulus project. *Atmospheric Science Paper No. 419*, Colorado State University, Ft. Collins CO. U.S.A.

- [16] Sedunov, Yu. S., 1974: "Physics of drop formation in the atmosphere." Wiley, New York, 234 p.
- [17] Srivastava, R. C. and J. L. Coen, 1992: New explicit equations for the accurate calculation of the growth and evaporation of hydrometeors by the diffusion of water vapor. *J. Atmos. Sci.*, **49**, 1643-1651.
- [18] Twomey, S., 1974: Pollution and the planetary albedo. *Atmos. Environ.*, **8**, 1251-1256.
- [19] Twomey, S., 1977: The influence of pollution on the shortwave albedo of clouds. *J. Atmos. Sci.*, **34**, 1149-1152.

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Ammonium Sulfate Equilibrium Curves

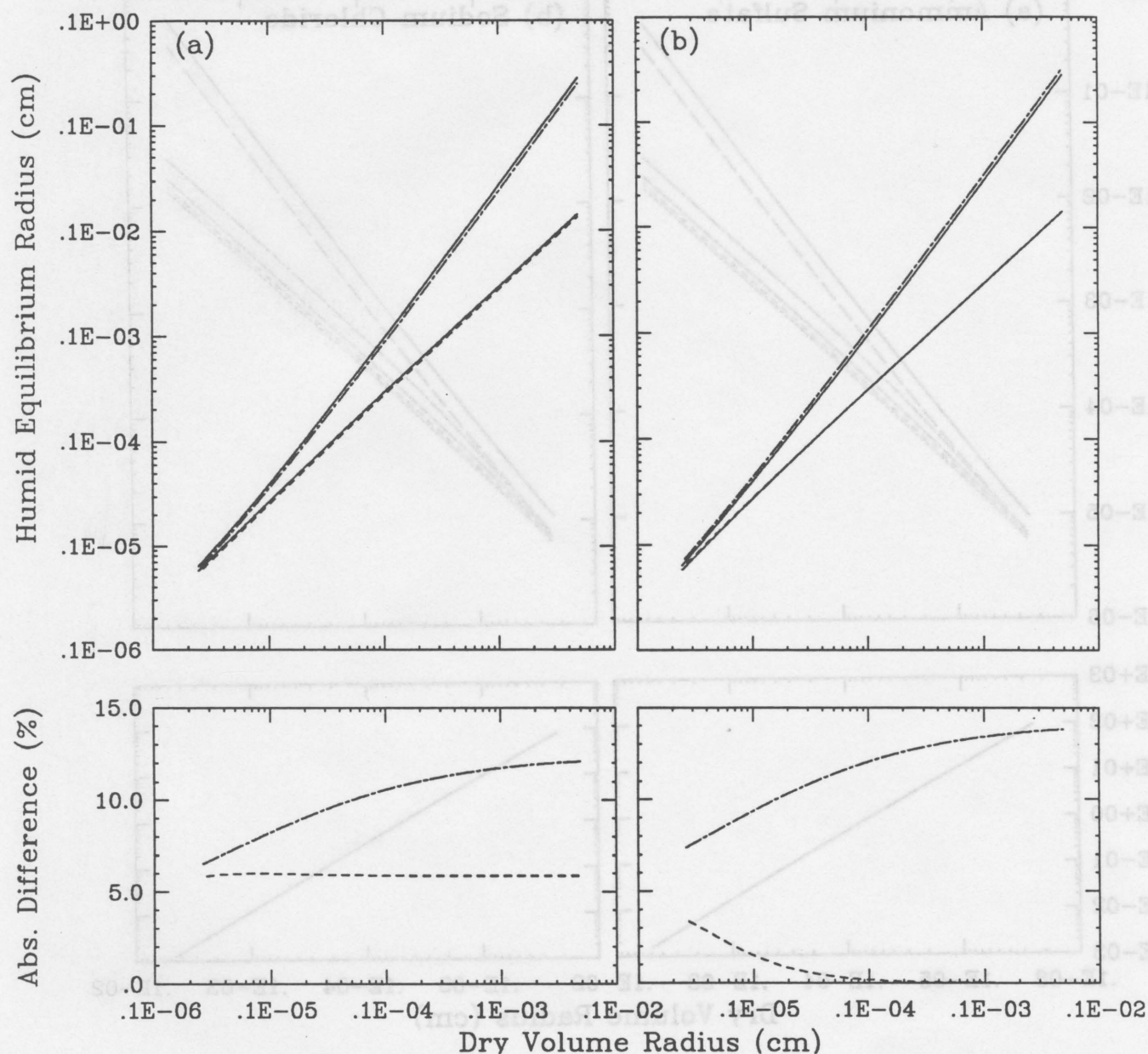


Figure 1: Dependence of equilibrium curves on assumptions of surface tension and Raoult's law unmodified by solute concentrations. Figure (a) Ammonium sulfate equilibrium sensitivity tests to variations in β . Solid lines represent ideal solutions, dashed-dot and short-dash lines represents solutions for $\beta = 0.767\beta_{ideal}$. Upper lines represent $\gamma = 0$ solution, while lower lines is for $RH = 95\%$. Figure (b) same as Figure (a) except for $\alpha = 0.767\alpha_{ideal}$.

Equilibrium Curves

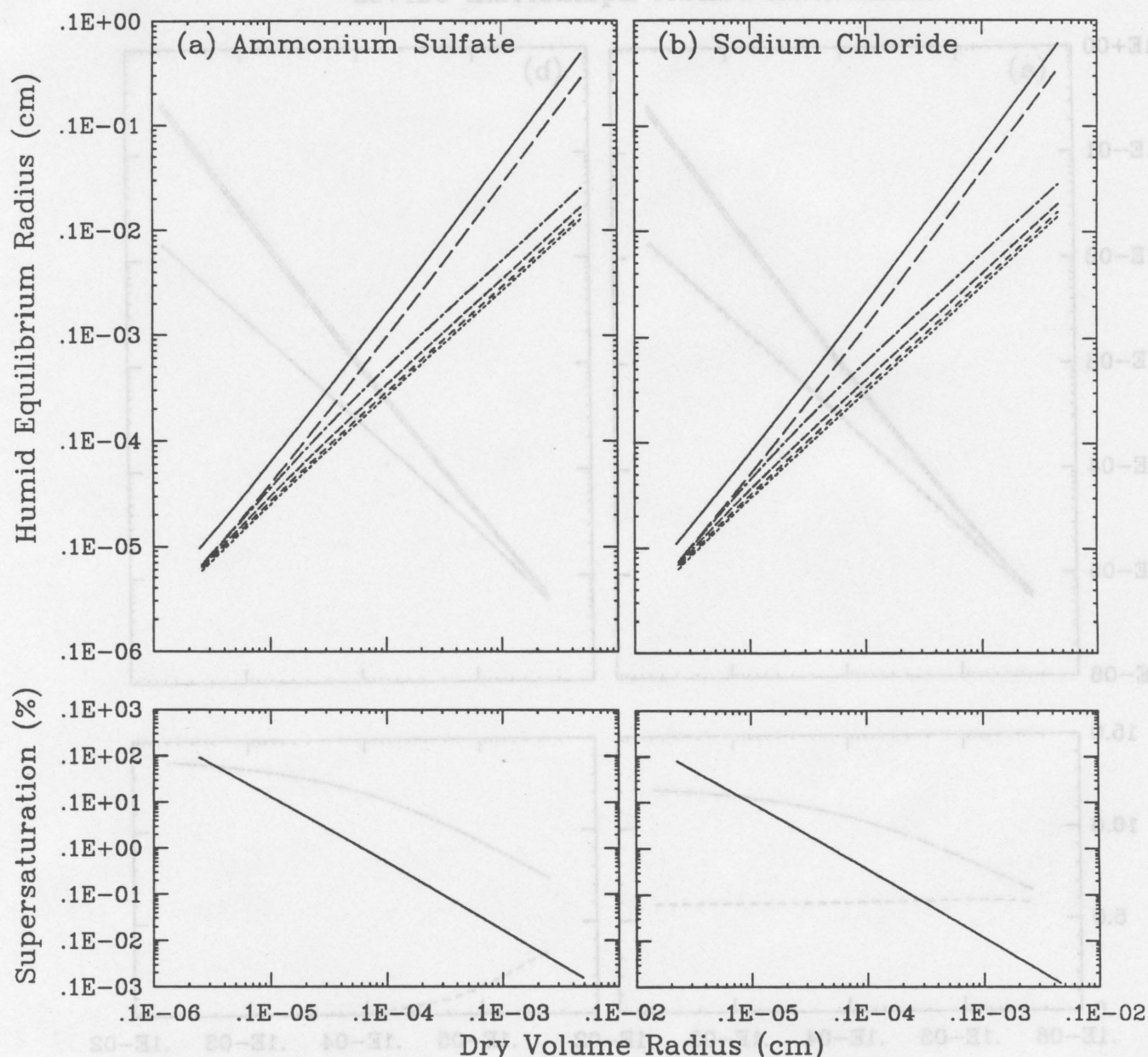


Figure 2: Equilibrium Curves for: (a) Ammonium Sulphate; and (b) Sodium Chloride. The solid line represents the equilibrium size at the activation supersaturation (which is plotted below each figure), following that successive lines represent $RH = 100\%$, 99% , 95% , 85% , 80% equilibrium curves.

Ammonium Sulfate Equilibrium Curves

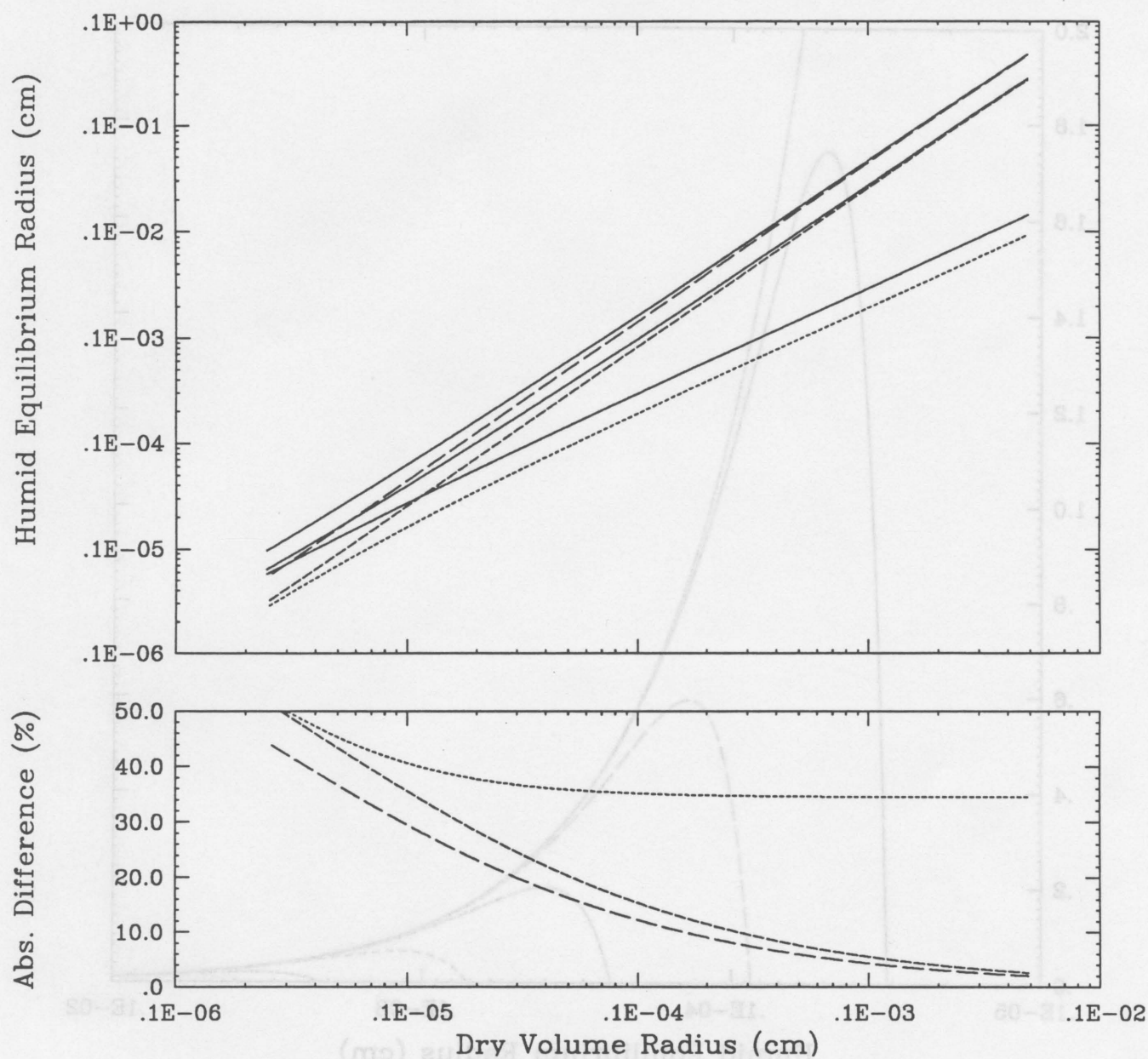


Figure 3: Dependence of equilibrium curves on the assumption that a can be neglected in comparison to r in the denominator of the β (solute) term of Equation (11). The lines successively represent the activation, $\gamma = 0$, and $RH = 95\%$ equilibrium curves. Solid lines are the exact solutions while dashed and dotted lines represent solutions as predicted by approximations.

Ammonium Sulfate Equilibrium Curves

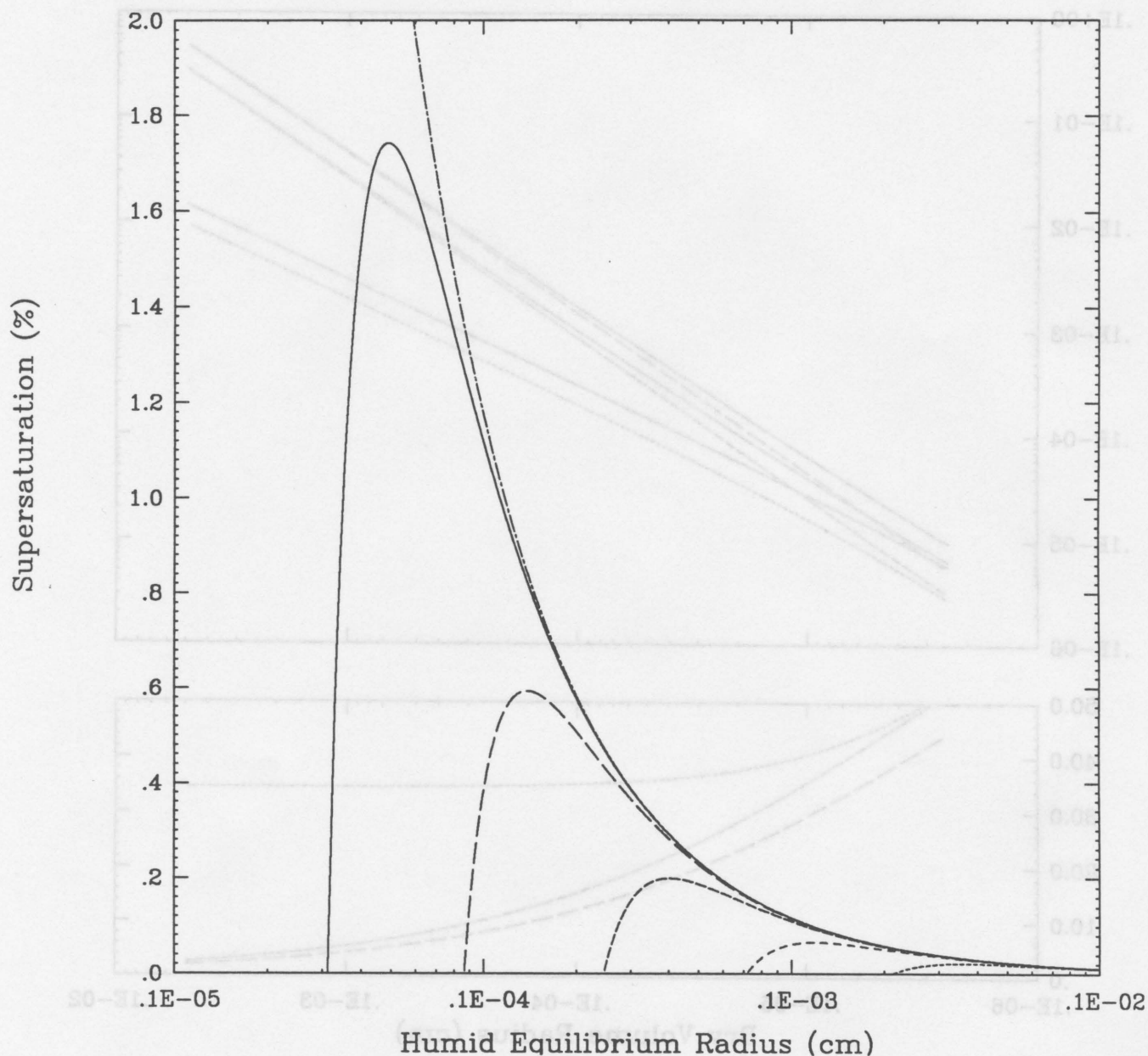


Figure 4: Köhler curves for drops containing varying amounts of Ammonium Sulfate. Successive curves represent Ammonium Sulfate dry masses of 4×10^{-18} , 4×10^{-17} , 4×10^{-16} , 4×10^{-15} , 4×10^{-14} grams. Or alternatively 8.14×10^{-3} , 1.75×10^{-2} , 3.78×10^{-2} , 8.14×10^{-2} , 1.75×10^{-1} microns in terms of dry radii. The longdash-dot line represents the Kelvin curve for the variation of equilibrium vapor pressure over an aqueous solution drop for pure water.

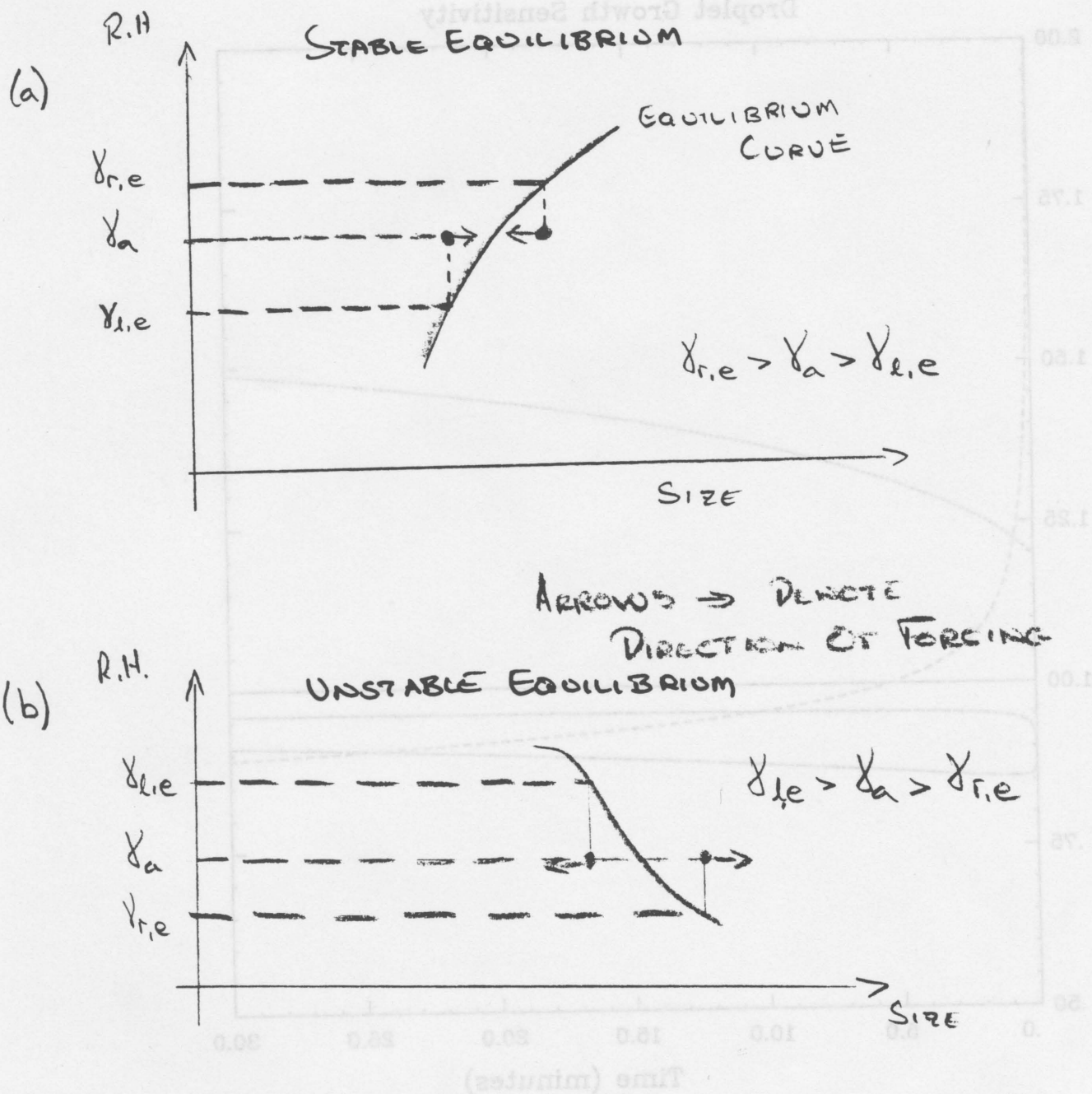


Figure 5: A schematic cartoon of the forcing associated with stable and unstable equilibrium for solution drops

Droplet Growth Sensitivity

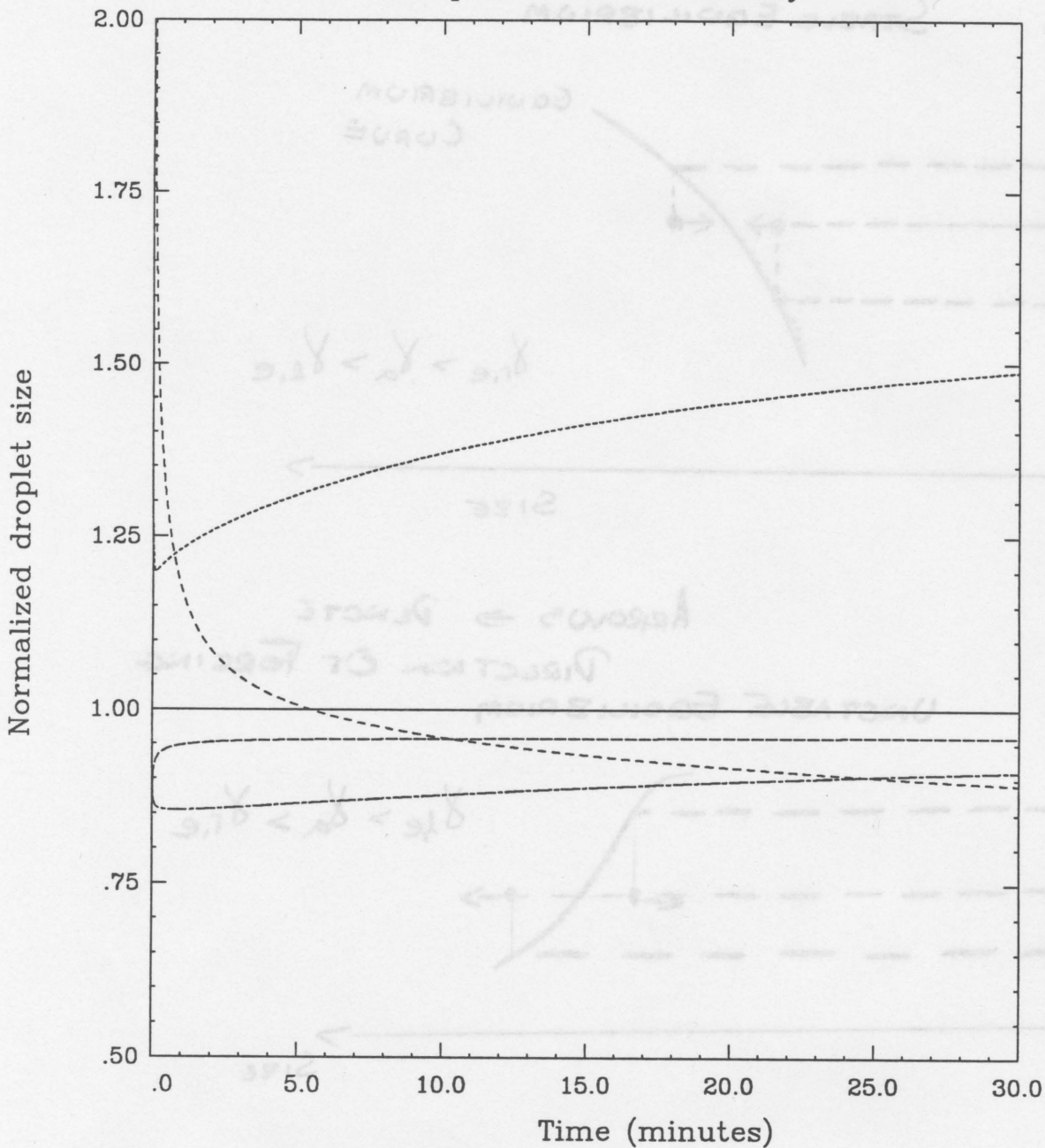


Figure 6: Sensitivity of droplet growth to various approximations of the droplet growth equation. The solid line represents the baseline which is the normalized growth of a sodium chloride nuclei at 0 °C, with an initial radius of 0.75 μm . The long dashed line with short spacing between dashes represents droplet growth with the constant density assumption. The dash-dot line represents the relative growth for an ammonium sulfate CCN, under similar conditions. The medium dash line represents the effect of assumptions about the diffusivity parameters (i.e., influence of neglect of gas kinetic parameters) on droplet growth. Lastly the short dashed line represents the growth behavior of the control droplet at 13 /deg C.

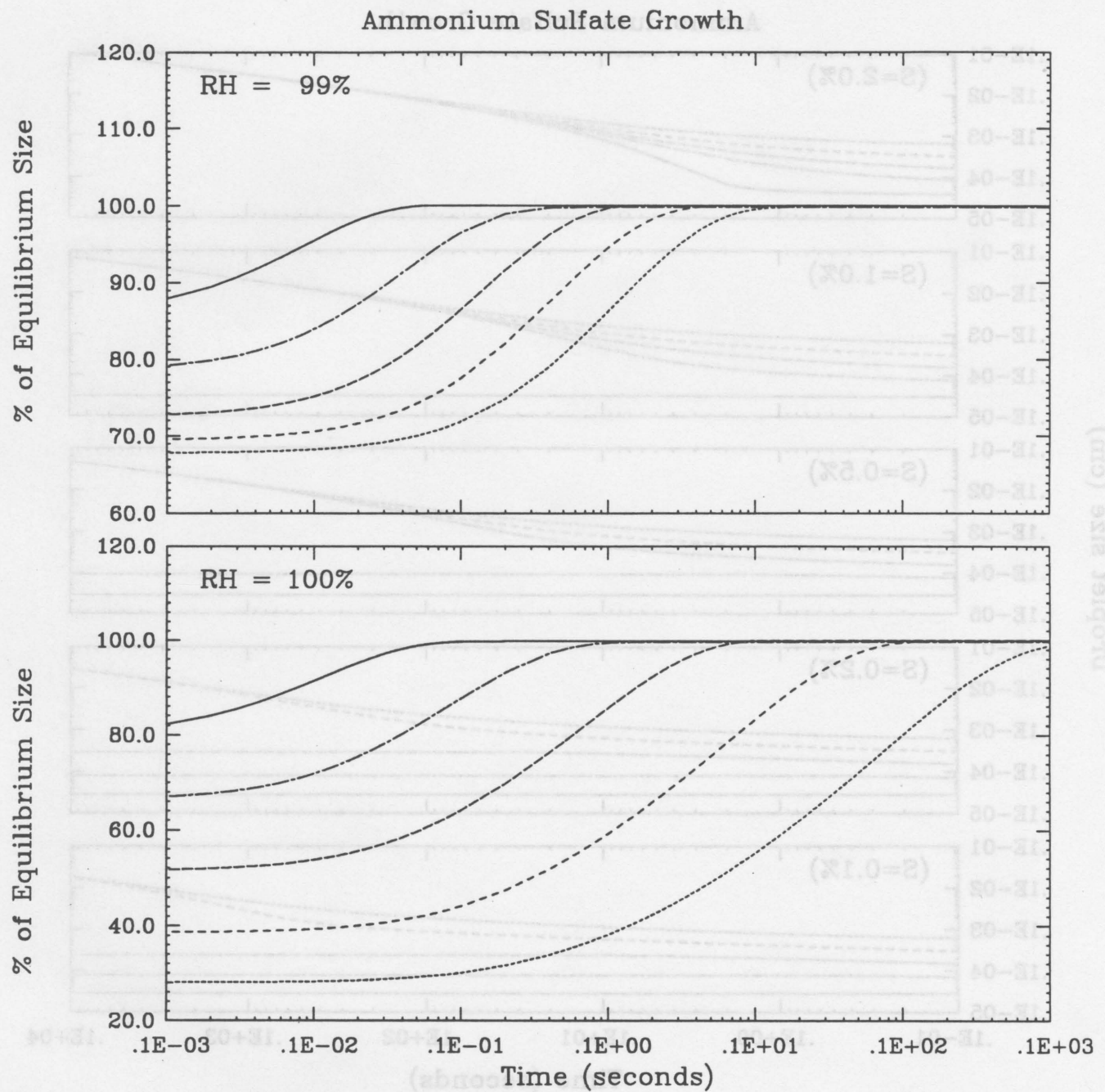


Figure 7: Solution drops with concentrations of ammonium sulfate as given for the 5 categories of CCN in Tables 1 and 2. Ratio of size to equilibrium size vs. time in: (a) 99 % relative humidity environment; (b) 100 % relative humidity environment

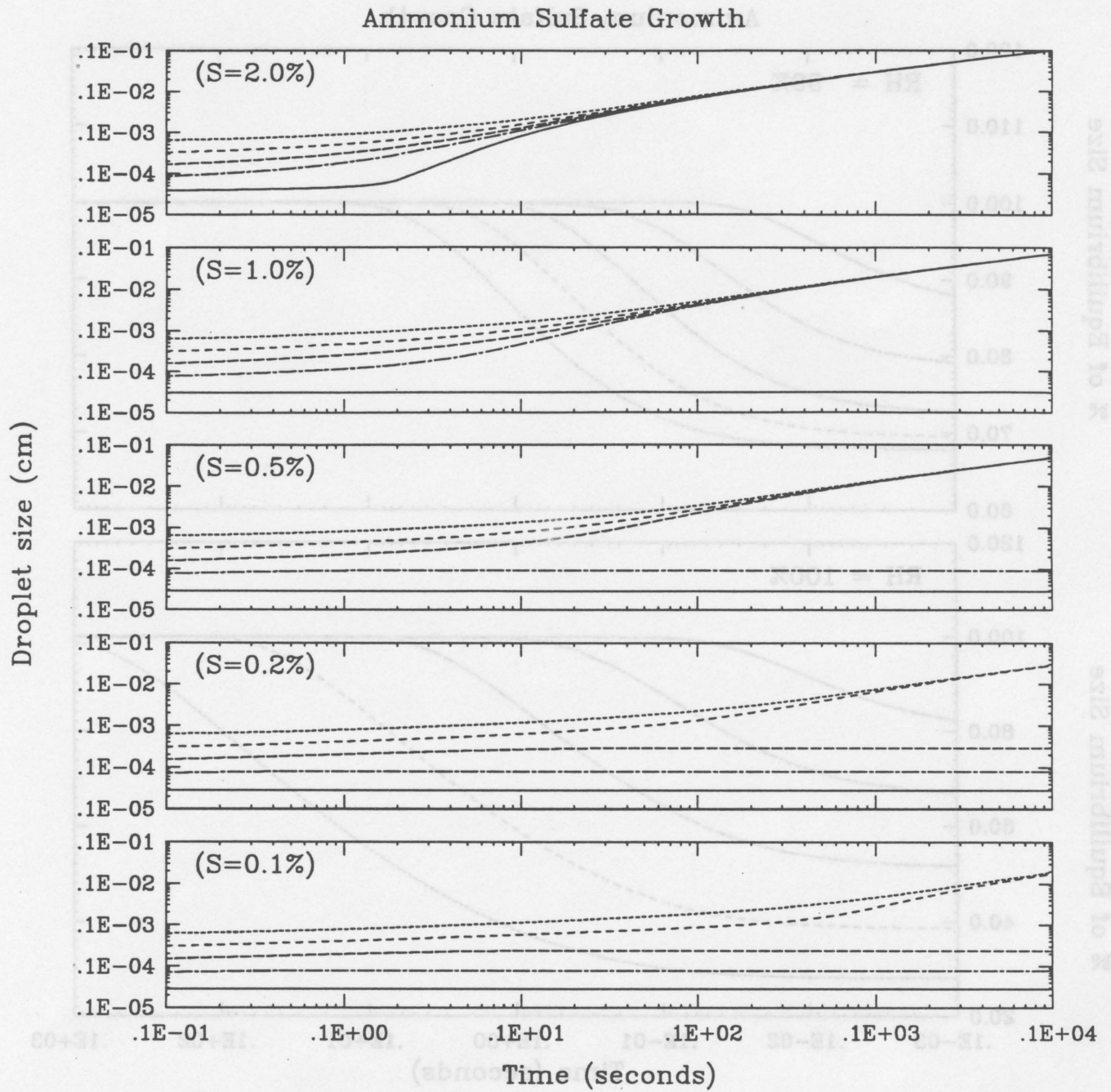


Figure 8: Diffusional growth rates as a function of time for the individual solution drops of Table 1 in five different constant supersaturation environments

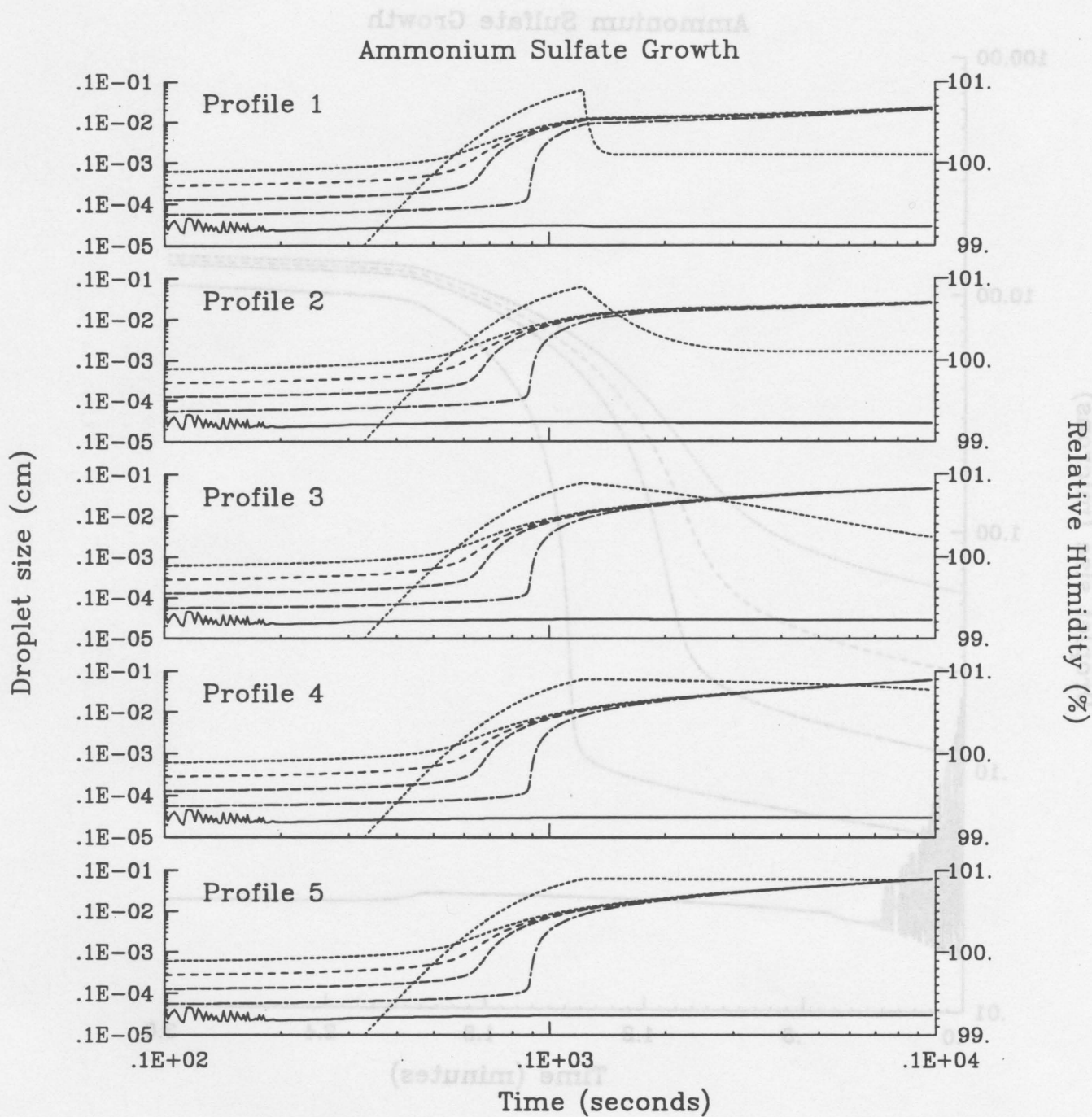


Figure 9: Diffusional growth rates as a function of time for the individual solution drops of Table 1 in five different time varying supersaturation environments, all with a maximum supersaturation of 1%. Compare with previous figure.

Ammonium Sulfate Growth

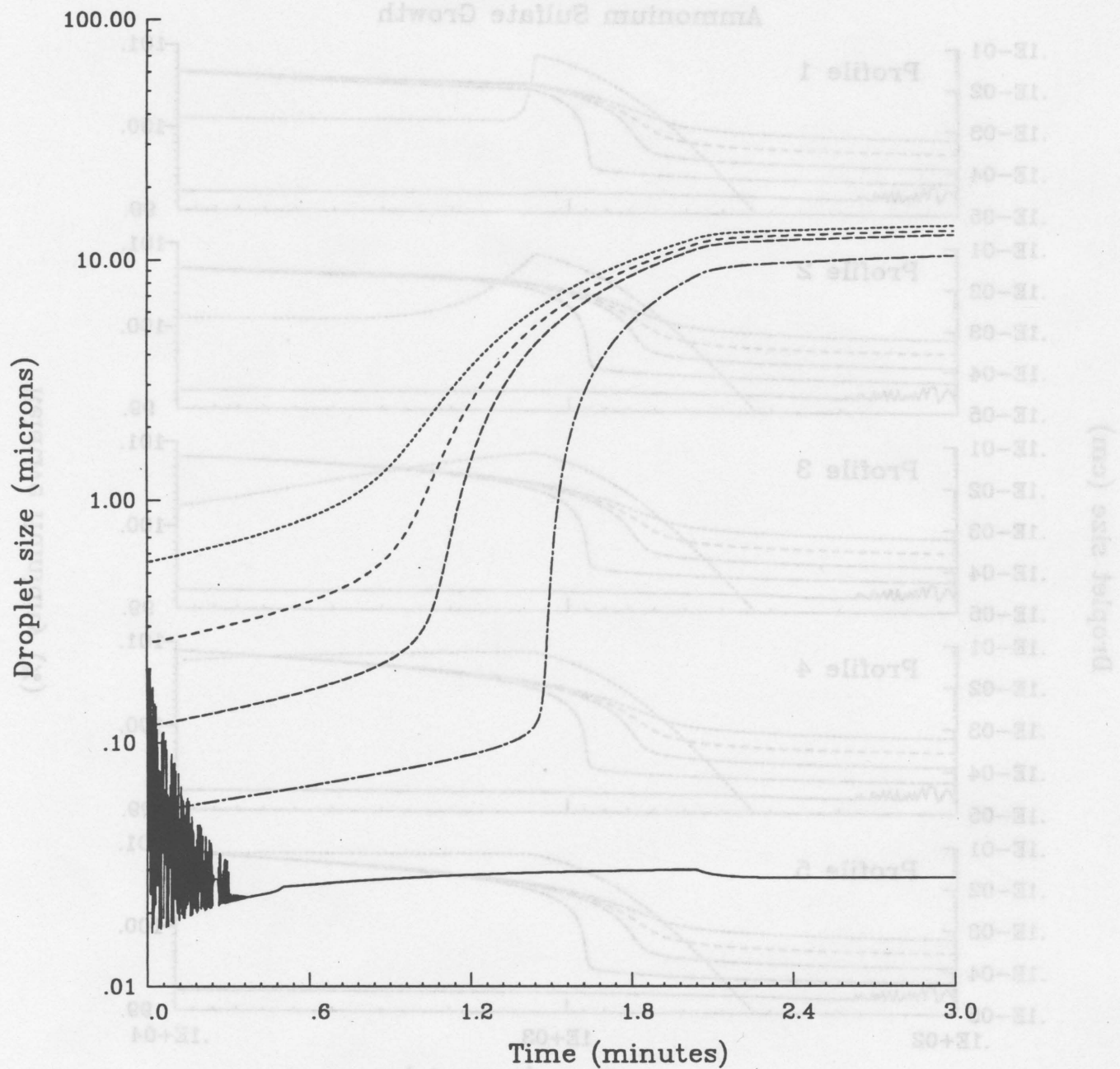


Figure 10: Diffusional growth rates as a function of time for the individual solution drops of Table 1 in the time varying supersaturation environment given by Profile 1 in Figure (9). The linear time scale gives a better overview of the droplet activation process. The oscillations associated with the growth trajectory of CCN1 are purely numerical modes and are discussed in the text.