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Köhler equation for finite systems: A simple estimation of possible condensation mechanisms in aircraft contrails

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Abstract. A generalization of the Köhler equation for systems with a limited amount of available water vapor is presented. Following the classical nucleation theory, a condensation process on soluble particles is discussed under isothermal-isochoric conditions. The resulting generalization of the Köhler equation deviates from the classical approach for droplets with radius larger than the critical radius. An additional minimum in the Köhler curve can be determined describing the effect of water limitation. The presented theory is applied for the estimation of possible water condensation processes during the formation of aircraft contrails. In particular, three different kinds of condensation centers (soot, soot covered with sulfuric acid, and pure H_2O/H_2SO_4 droplets) are compared with respect to the critical conditions which are necessary for their activation and with respect to their suitability for water uptake during condensation processes in the plume. Based on such investigations, soot particles with or without sulfuric acid can be easier activated than small H_2O/H_2SO_4 droplets for atmospheric situations where jets get supersaturated with respect to water and, consequently, may lead to sufficiently large frozen particles. If the plume is undersaturated with respect to water, there is no difference, at least in view of the water condensation processes, between the highly concentrated H_2O/H_2SO_4 droplets and soot particles with or without sulfuric acid.

1. Introduction

A derivation of the equilibrium supersaturation curves for soluble particle was first presented by *Köhler* [1921a, b, 1949]. Using the concept of classical nucleation theory, he discussed the homogeneous condensation of water droplets on soluble particles in terms of the Gibbs free energy ΔG. The classical nucleation theory and its extensions [see, e.g., *Becker and Döring*, 1935; *Volmer*, 1939] are valid for isothermal-isobaric conditions, i.e., for systems where the depletion of water vapor during the nucleation process can be neglected. This assumption can be violated in systems containing large numbers of condensation nuclei (CN). An example of such situation can be found in clouds or fogs or during the formation of aircraft contrails.

One possibility for taking into account this effect is to consider nucleation and condensation processes under isothermal-isochoric conditions, i.e. in a closed (finite) system with a fixed volume [*Vogelsberger*, 1977, 1985]. In such a system, in which the total amount of water is constant, the Helmholtz free energy ΔF is an adequate thermodynamical potential. In the next section we apply the methods proposed by *Vogelsberger* [1977, 1985] to a system containing soluble condensation nuclei. In particular, an appropriate Helmholtz free energy ΔF will be constructed. The extrema of this function with respect to the condensed water mass (or droplet radius) can be understood as equilibrium states of the considered (closed) system. For different water saturation ratios they lead to an equilibrium curve generalizing the classical Köhler approach [e.g., *Byers*, 1978; *Pruppacher and Klett*, 1978] to isothermal-isochoric systems. To study the effect of limitation of water vapor in a closed system, we discuss the condensation of water on H_2SO_4-H_2O droplets in a system characterized by different number densities of such droplets. Then we generalize the presented theory to heterogeneous processes on wettable but completely water insoluble particles.

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To give an application of the isochoric Köhler equation, different condensation mechanisms in an aircraft contrail are discussed. In contrast to the extensive description given previously [e.g., *Kärcher et al.*, 1995; *Zhao and Turco*, 1995; *Schumann et al.*, 1996], we carry out a simple energetic estimation of possible condensation processes of water vapor during the contrail formation. The conclusions are collected in the last section.

2. Köhler Equation for Finite Systems

Consider a closed system with a temperature T composed of dry air with a partial pressure p_a^g, water vapor with a partial pressure p_w^g, and M equal and homogeneously distributed droplets with the number density N_c (unimodal spectrum). Neglecting the partial pressure of the condensation centers, the total pressure of the system is given by $p_{\text{tot}} = p_a^g + p_w^g$. Each droplet is assumed to be a liquid solution which consists of water and (partially) dissociated acid or salt. Pure solute in the droplet is characterized by the mass $m_s = n_{s0} M_s$ where n_{s0} and M_s are the mole number and the molar mass of the solute, respectively. Furthermore, n_w denotes the mole number of water in the droplet, M_w is the corresponding molar mass.

Due to homogeneity, one can replace the M-particle system by a system containing only one condensation center in volume $V_c := 1/N_c$ (see Figure 1). Consequently, the complete set of variables describing the state of the system is: T, p_{tot}, p_w^g, n_{s0}, and n_w.

Now we discuss the condensation process of water on one soluble nucleus with a constant mole number n_{s0} for constant values of temperature T, total pressure p_{tot} and amount of water in the volume V_c. Due to the constant temperature and limited water amount, we denote the considered processes as isotherm-isochoric with respect to water vapor or, abbreviated, isotherm-isochoric. In particular, the following two states of the system are considered: The initial state (index i) consists of a pure solute ($n_w = 0$) surrounded by water vapor with the pressure $p_w^{g_i}$. In the final equilibrium state (index f) the solution droplet has the mole numbers n_w and n_{s0}, where n_w represents the mole number of water transfered from the vapor phase to the solution droplet. Neglecting the droplet volume, the final water pressure p_w^{gf} amounts to

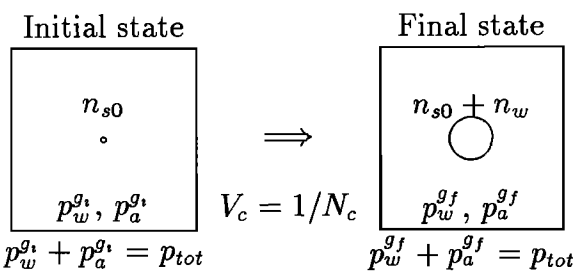

Figure 1. Description of the notation used.

$$p_w^{gf} = p_w^{g_i}\left(1 - \frac{n_w}{n_w^{g_i}}\right), \qquad n_w^{g_i} = \frac{p_w^{g_i} V_c}{RT} = \frac{p_w^{g_i}}{RTN_c}. \quad (1)$$

Here, $n_w^{g_i}$ is the initial mole number of water vapor, which can be expressed in terms of $p_w^{g_i}$ by use of the ideal gas equation. R is the universal gas constant.

It should be emphasized that, in contrast to the binary nucleation theory [*Nair and Vohra*, 1975; *Yue*, 1979; *Yue and Hamill*, 1979], we neglect the partial pressure of the solute in the gaseous state as well as the exchange of the solute particles between the gaseous and liquid state. This assumption is motivated by the observation that for many atmospheric situations the partial pressure of water vapor overcomes the partial pressure of solute by several orders of magnitude and, consequently, the condensation of water vapor dominates the droplet growth.

Now, we discuss the condensation process of water on one soluble nucleus under isothermal-isochoric conditions, i.e., for constant temperature T and volume V_c. Then, the Helmholtz free energy of condensation ΔF is given by [*Vogelsberger*, 1977]

$$\Delta F = \Delta F_1 + \Delta F_2 + F_{\text{surf}} \quad (2)$$

with

$$\begin{aligned} \Delta F_1 &= n_w^{g_i} RT \ln \frac{p_w^l}{p_w^{g_i}} + n_w RT \\ &\quad + (n_w^{g_i} - n_w) RT \ln \frac{p_w^{gf}}{p_w^l} \\ \Delta F_2 &= RT(n_w \ln a_w + n_{s0} \ln a_s) \end{aligned} \quad (3)$$

where ΔF_1 denotes the reversible energy change during the water condensation on a dry particle and ΔF_2 describes the mixing contribution of ΔF. In particular, p_w^l is the equilibrium pressure of water over a flat water surface, and a_w and a_s are water and solute activities, respectively. F_{surf} denotes the free energy of the surface. The individual terms of ΔF_1 describe the expansion (or compression) of the initial water vapor from the initial pressure $p_w^{g_i}$ to the equilibrium pressure p_w^l, the condensation of water (here we neglect the volume of the liquid droplet compared with its volume in the gaseous state), and the expansion (or compression) of the water vapor from the equilibrium pressure p_w^l to the final pressure p_w^{gf}.

Then, for a spherical droplet with radius r, the Helmholtz free energy (2) can be rewritten as

$$\begin{aligned} \frac{\Delta F}{RT} &= n_w\left(1 - \ln \frac{S_w}{a_w}\right) + n_{s0} \ln a_s \\ &\quad + (n_w^{g_i} - n_w) \ln\left(1 - \frac{n_w}{n_w^{g_i}}\right) + \frac{4\pi\sigma r^2}{RT} \end{aligned} \quad (4)$$

with

$$\frac{4\pi}{3} r^3 \rho = n_w M_w + n_{s0} M_s \quad (5)$$

and the water saturation ratio $S_w := p_w^{g_i}/p_w^l$. Here, ρ

and σ are the density and the surface tension of the solution. Furthermore, the quantities σ, ρ, a_w, and a_s depend on n_w and n_{s0} only through the mass fraction x of the solute in the solution defined by

$$x := \frac{M_s n_{s0}}{M_w n_w + M_s n_{s0}}. \tag{6}$$

Assuming that only n_w is a free variable of the considered system, i.e., $\Delta F = \Delta F(n_w)$, the stable and metastable states can be determined from the necessary condition for the existence of extrema of ΔF. Consequently, the derivation of (4) with respect to n_w together with the Gibbs-Duhem relation leads to a (generalized) Köhler equation for isothermal-isochoric systems. Following the methods developed by *Nair and Vohra* [1975], *Yue* [1979], *Yue and Hamill* [1979], and *Konopka* [1996], one obtains

$$RT \ln \frac{S_w}{a_w}\left(1 - \frac{n_w}{n_w^{g,}}\right) = \frac{2M_w\sigma}{r\rho}\left(1 + \frac{x}{\rho}\frac{d\rho}{dx} - \frac{3}{2}\frac{x}{\sigma}\frac{d\sigma}{dx}\right), \tag{7}$$

where r and n_w are connected through relation (5). If one assumes that the presented theory should be consistent with the Gibb's adsorption equation [*Wilemski*, 1984], then the surface tension σ does not depend on the composition. Note that for $V \to \infty$, and, consequently, $n_w^{g,} \to \infty$, equation (7) reduces to the Köhler equation for isothermal-isobaric systems as given, for example by *Yue* [1979], *Yue and Hamill* [1979], and *Konopka* [1996].

Assuming ρ =const and σ =const, one obtains from (7)

$$\ln S_w \left(1 - \frac{n_w}{n_w^{g,}}\right) = \frac{2M_w\sigma}{r\rho RT} - \ln a_w, \tag{8}$$

For highly diluted electrolytes, the (ideal) approximation

$$\ln a_w = \ln \frac{n_w}{n_w + \nu_s n_{s0}} \approx -\frac{\nu_s n_{s0}}{n_w}, \qquad \frac{4\pi}{3} r^3 \rho_w \approx n_w M_w \tag{9}$$

can be used, where ρ_w denotes the density of water and ν_s is a factor which describes the number of molecules and ions in a partially dissociated electrolyte. For a completely dissociated electrolyte the relation $\nu_s = \sum_{i=1}^{n} \nu_i$ holds, where the vector $\{\nu_i\}$ describes the stoichiometric coefficients of the particular ions of the solute in question. Then equation (8) can be transformed into the well-known form of the Köhler equation,

$$\ln(S_w - \alpha r^3) = \frac{2M_w\sigma}{RTr\rho_w} - \frac{3M_w\nu_s n_{s0}}{4\pi\rho_w r^3}, \qquad \alpha = \frac{4\pi\rho_w RTN_c}{3M_w p_w^l} \tag{10}$$

where, in contrast to the classical Köhler equation [see, e.g., *Pruppacher and Klett*, 1978], S_w is corrected by the term αr^3.

Now, we apply our results to a H_2SO_4-H_2O system by $T = 223$ K, i.e., for temperatures which are typical for the upper troposphere. The experimental data for the water activity a_w are taken from *Nair and Vohra* [1975]. Furthermore, we neglect the dependence of density ρ and surface tension σ on the mass fraction x and use [*Resch*, 1995]

$$\rho = \rho(x = 0.1) = 1.045 \text{ g/cm}^3, \qquad \sigma = \sigma(x = 0.1) = 84.5 \text{ dyn/cm}. \tag{11}$$

In particular, we are interested in the meaning and in the importance of the isochoric correction α compared with the classical, i.e., isobaric approach. For this purpose, we consider the (isochoric) Köhler equation (8) for a H_2SO_4-H_2O droplet containing 10^4 H_2SO_4 molecules (i.e., $m_s = 1.6\times10^{-21}$ kg) and undergoing condensation in a system with two different densities of condensation centers $N_c = 10^{10}$ and $N_c = 10^{16}$ m^{-3}, respectively.

The resulting curves, i.e., S_w (or S_i, i.e., ice supersaturation) versus r, are plotted in Figure 2. Here the solid dashed-dotted solid and solid curves correspond to $N_c = 10^{10}$ and $N_c = 10^{16}$ m^{-3}, respectively. The classical (isobaric) Köhler equation can be formally derived from (8) assuming $1 - n_w/n_w^{g,} \approx 1$ and consequently does not depend on N_c. The corresponding dashed line is in accordance with the isochoric curve for $N_c = 10^{10}$ and r smaller than approximately 200 nm. For $r > 200$ nm the isochoric curves totally deviate from isobaric description. In the case of $N_c = 10^{16}$ m^{-3}, the deviation of the classical approach is given for all values of r.

It should be emphasized that the analysis of the Köhler equation, i.e., the possible r and S_w values de-

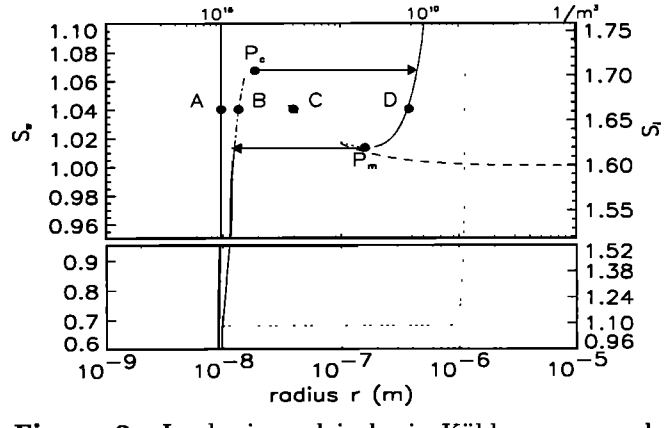

Figure 2. Isochoric and isobaric Köhler curves calculated for a droplet containing 10^4 H_2SO_4 molecules. The solid dashed-dotted solid and solid lines denote the isochoric curves calculated for $N_c = 10^{10}$ and 10^{16} m^{-3}, respectively. The isobaric (i.e., classical) curve agree with the isochoric case for $N_c = 10^{10}$ m^{-3} and r smaller than approximately 200 nm. For $r > 200$ nm the dashed line describes the classical case. For explanation of the remaining notation, see text.

scribing the equilibrium states of the droplet, does not distinguish between the energetically stable, metastable, or unstable states. The stability of a relative minimum of ΔF (or ΔG) depends on its relative energy value compared to other minima of ΔF (or ΔG) and on the height of the energy barriers separating the considered minimum from the remaining stable or metastable states. Consequently, in order to decide which form of stability corresponds to the particular points of the Köhler curve, the thermodynamical potential used has to be taken into account [*Reiss and Koper*, 1995]. Based on such considerations, the solid, dash-dotted, and dotted parts of the isochoric Köhler curves in Figure 2 denote the stable, metastable, and unstable states (energy barrier), respectively.

In order to illustrate this interpretation, we consider an atmospheric state with $S_w = 1.04$ and $N_c = 10^{10}$ m^{-3} (see Figure 2). In the isobaric case two equilibrium states are possible: the metastable state B and the unstable state C. The latter one describes the absolute maximum of ΔF and separates a stable (nonactivated) droplet in state B from the region where the droplet growth is limited only by the amount of available water.

Generally [see, e.g., *Pruppacher and Klett*, 1978; *Byers*, 1978], the droplet radius r_c denoting the maximum of the (isobaric) Köhler curve $P_c = (r_c, S_c)$ as well as the corresponding value of $S_c = S_w(r_c)$ are understood as the critical radius or the critical saturation which, if exceeded, leads to an unlimited droplet's growth. This interpretation requires revision in systems with limited water vapor reservoir. Here the isochoric Köhler equation should be used leading to additional stable states of ΔF. For $N_c = 10^{10}$ the stable state D is possible; for $N_c = 10^{16}$ the droplet can only exist in the stable state A. Both states are a consequence of the described water limitation or, in other words, of the used isochoric correction in the Köhler equation. Their existence changes the usual interpretation of the Köhler equation for all relevant values of S_w.

Finally, another important difference between the isochoric and isobaric approach is the meaning of the critical saturation. The classical interpretation [see, e.g., *Pruppacher and Klett*, 1978] predicts an "unlimited droplet growth" with $r > r_c$ for $S_w > S_c$, i.e., for the so-called activated droplets. To describe the details of the growth process, different kinetic theories have to be taken into account. Here, i.e., by use of the isochoric Köhler equation, the final state of the droplet growth can be described in terms of an additional equilibrium state which, e.g., for $N_c = 10^{10}$ m^{-3}, is given by the end of the upper arrow (see Figure 2). Similarly, for $1 < S_w < S_m$ with $P_m = (r_m, S_m)$ a liquid droplet with radius r_m can spontaneously evaporate along the lower arrow. Consequently, the isochoric Köhler equation constitutes a theoretical framework within the hysteresis effects of droplet growth and evaporation can be discussed.

Of course, the presented theory is also applicable for frozen droplets if the ice crystals can be approximately described as spherical particles with an appropriate surface tension. Furthermore, S_w has to be replaced by S_i, and all the thermodynamical equilibrium data have to be related on ice. To estimate the $r - S_w$ domain in which the frozen droplets can exist, the dotted lines calculated for $p_w^{gf} = 0$ and $S_i = 1$ are plotted in Figure 2. Consequently, the possible states of frozen droplets are bounded by the isotherm-isochoric Köhler equations and both these curves.

3. Heterogeneous Condensation

In many cases the condensation of water on soluble particles can be significantly influenced by the presence of water-insoluble but wettable heterogeneous surfaces [*Pruppacher and Klett*, 1978]. In the following, we generalize the results of the previous section to condensation processes in which each condensation center consists of a pure solute together with a solid, water-insoluble, and spherical particle with radius R. Here, two cases are discussed in which the solid particle is either completely or partially included in the solution droplet (see Figure 3). In the latter case, as a consequence of the Young relation [see *Pruppacher and Klett*, 1978], the contact angle θ determines the contact surface.

To describe the heterogeneous condensation process, F_{surf} and equation (5) have to be modified, i.e.,

$$\begin{aligned} F_{\text{surf}} &= 4\pi r^2 f(r)\sigma, \\ \frac{4\pi}{3} r^3 g(r)\rho &= n_w M_w + n_{s0} M_s. \end{aligned} \tag{12}$$

where the functions f and g depend on the geometry considered. According to *Pruppacher and Klett* [1978],

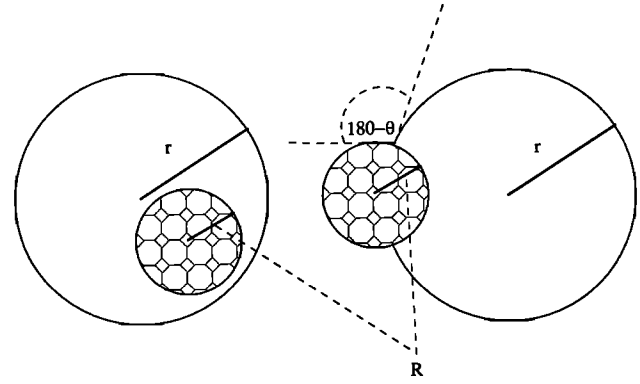

Figure 3. Heterogeneous condensation on spherical, wettable but completely water-insoluble particle with radius R. (left) The solution droplet with radius r completely includes the particle. (right) The contact surface between the particle and the solution droplet is given through the contact angle θ.

one obtains for a convex contact surface

$$f(r) = \frac{1}{2}\left(1 - \cos\psi - y^2\cos\theta(1-\cos\vartheta)\right)$$
$$g(r) = \frac{1}{4}\left(2 - 3\cos\psi + \cos^3\psi - \right. \qquad (13)$$
$$\left. - y^3\left(2 - 3\cos\vartheta + \cos^3\vartheta\right)\right)$$

with

$$\cos\psi = \Phi^{-1}(y\cos\theta - 1),$$
$$\cos\vartheta = \Phi^{-1}(y - \cos\theta),$$
$$\Phi = (1 + y^2 - 2y\cos\theta)^{1/2}, \quad y = \frac{R}{r}. \qquad (14)$$

Here, θ denotes the contact angle with $0 \le \theta \le 180°$. For $\theta = 0$ and $r > R$ the solution droplets completely includes the particle. In particular, equations (13) simplify to

$$f(r) = 1 - y^2, \qquad g(r) = (1 - y^3). \qquad (15)$$

A straightforward calculation leads to an isothermal-isochoric Köhler equation for heterogeneous condensation processes on soluble particles which generalizes equation (7). It reads

$$RT\ln\frac{S_w}{a_w}\left(1 - \frac{n_w}{n_w^{g_i}}\right) = \qquad (16)$$
$$k\frac{2M_w\sigma}{r\rho}\left(1 + \frac{x}{\rho}\frac{d\rho}{dx} - \frac{3}{2}\frac{xf}{\sigma kg}\frac{d\sigma}{dx}\right)$$

with

$$k = \frac{f + \frac{1}{2}rf'}{g + \frac{1}{3}rg'}. \qquad (17)$$

Here, f' and g' denote the derivatives with respect to r.

4. Formation of Contrails

Contrails from engine exhaust of high-flying aircraft may influence the climatological and chemical state of the atmosphere [*Schumann*, 1994; (*World Meteorological Organization)*, 1995]. As explained by *Appleman* [1953], contrails form when isobaric mixing between the hot and humid exhaust plume and cold ambient air leads to a mixture reaching saturation with respect to water so that cloud droplets form which then might freeze to form ice particles. In order to understand the droplets formation, the nucleation and condensation processes have to be studied.

Several recent studies suggest that about 0.5 to 2.0% of the emitted sulfur oxides are converted to sulfuric acid in the young exhaust plume, i.e., for plume age < 1 s [*Reiner and Arnold*, 1993; *Miake-Lye et al.*, 1993, 1994; *Kärcher et al.*, 1995]. One of the widely discussed nucleation mechanisms is the binary nucleation of sulfuric acid with water and the subsequent homogeneous growth of the droplets characterized by a rapid water uptake [*Kärcher et al.*, 1995]. Another possibility is the binary heterogeneous nucleation of sulfuric acid with water on exhaust particles such as soot [*Zhao and Turco*, 1995; *Schumann et al.*, 1996]. Both nucleation mechanisms lead to particles which act as cloud condensation centers. For a sufficiently high water supersaturation they grow through water uptake, which is only limited by the available water content.

The aim of this section is to discuss the question whether and under which conditions the condensation of water vapor on soot particles with or without sulfuric acid seems to be more favorable than a homogeneous growth of H_2O/H_2SO_4 droplets. For this purpose, the isochoric Köhler equation derived in previous section is considered.

In particular, we confine our study to an air parcel on the jet axis at a time when the maximum possible relative humidity, $S_w^{\max}$, is reached. This value strongly depends on the amount of water vapor released by the engine, the ambient conditions, and on the expanding and cooling of the jet. Typically, $1 < S_w^{\max} < 2$ is reached at plume age $0.1 < t^{\max} < 1$ s and corresponds to jet diameter D between 2 and 3 m. Furthermore, we assume that in contrast to the total jet, the considered air parcel is in local equilibrium, and consequently, the discussed Köhler equation can be applied.

In the following, two different water condensation mechanisms in the air parcel are discussed: First, we study condensation of water on soot particles which surface may be covered, at least partially, with sulfuric acid. *Lammel and Novakov* [1995] have shown that the condensation abilities of chemically modified carbonaceous particles increases with increasing soluble mass fraction. CN containing soot and H_2SO_4 are expected in aircraft engine exhaust either as a consequence of sulfur uptake during the soot formation in the combustion chamber and its subsequent oxidation to H_2SO_4 or as a result of coagulation processes between soot and sulfuric acid molecules in the first tenth of a second behind the engine exit [*Zhao and Turco*, 1995]. Typically, one expects particle number density $N_{\text{soot}} \approx 10^{11}$ m^{-3}, soot radius of about 60 nm [*Schumann et al.*, 1996], and numbers of H_2SO_4 molecules per soot particle varying between 0 and 10^4. From the one side, the considered number of H_2SO_4 molecules is consistent with the number of SO_2 particles converted to H_2SO_4 [*Kärcher et al.*, 1995]. From the other side, if one assumes that soot properties are similar to those of the activated carbon, then the formation of H_2SO_4 on soot may be explained via adsorption of SO_2, oxidation of SO_2 to SO_3 and subsequent reaction with water vapor to H_2SO_4. According to *Moreno-Castilla et al.* [1993], 1 g of weakly activated carbon adsorbs about 50 mg SO_2 (saturation value) at

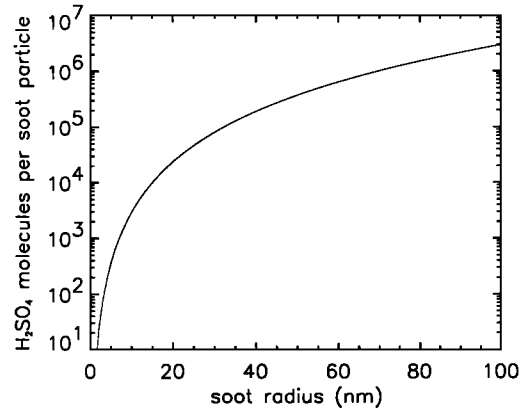

Figure 4. Maximal number of adsorbed H_2SO_4 molecules per soot particle (considered as weakly activated carbon) versus soot radius.

$T = 273$ K. In such a case, assuming a complete conversion of adsorbed SO_2 to H_2SO_4, the maximal number of H_2SO_4 molecules per soot particle can be estimated (Figure 4), indicating that soot in form of activated carbon may significantly adsorb sulfur components.

Second, we consider condensation on homogeneous H_2SO_4/H_2O droplets formed from subnanometer germs (via binary nucleation theory) through quick coagulation processes during the first 0.1 s of dispersion. According to *Kärcher et al.* [1995], more than 10^{14} such droplets with less than 50 H_2SO_4 molecules per droplet have to be expected at t^{max}.

Assuming that coagulation of the described condensation centers is mainly due to Brownian motion [*Pruppacher and Klett*, 1978], one can estimate that for both types of condensation centers such processes are negligible at t^{max} (the typical coagulation times calculated for these processes do not exceed 0.1 s). Consequently, the H_2SO_4 content in the droplets or on the soot particles is approximately constant; the two kinds of condensation centers considered can grow only by water uptake.

Now we apply our study to two different ranges of water saturation ratio S_w^{max}, i.e., $S_w^{max} \geq 1$ and $S_w^{max} < 1$.

$\mathbf{S_w^{max} > 1}$. Here the behavior of the air parcel is mainly determined by the values of S_c and S_m. In Figure 5, S_c calculated from (8) is plotted versus number of H_2SO_4 particles in the droplet (solid line). The dotted line denotes the same function determined from the ideal approximation (10). The remaining lines describe the change of the critical saturation if the heterogeneous correction, given by equation (17), is taken into account.

One concludes that droplets without soot containing less than 100 H_2SO_4 molecules can be activated for $S_w^{max} > 2$, i.e., for values which can be reached only for exceptional atmospheric situations. On the other side, soot can significantly decrease the values of S_c. In particular, in the case of completely included soot the droplet activation may occur for $S_c > 1.05$, whereas in the case of partially wetted soot, the critical values are higher.

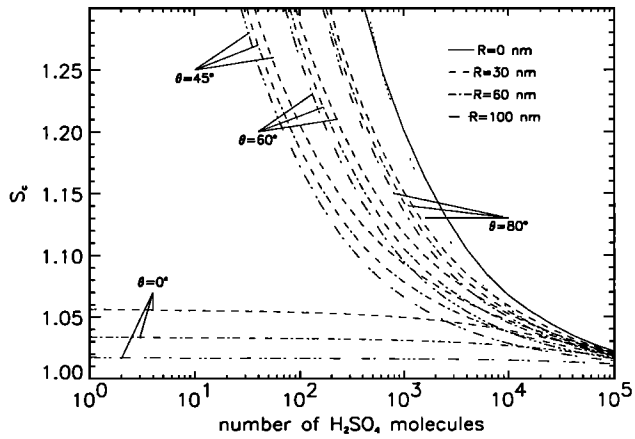

Figure 5. Critical saturation S_c necessary for homogeneous ($R = 0$) and heterogeneous activation of the droplet versus number of H_2SO_4 molecules contained in the droplet. In the homogeneous case the solid line is calculated from (8), the dotted line describes the ideal approximation (10). The dashed, dot-dashed, and triple dot-dashed lines denote the critical saturation S_c for soot radii $R = 30$, 60, and 100 nm, respectively, and are calculated for contact angles $\theta = 0$ (soot inclusion), 45°, 60°, and 80°.

Another point of view, connected to the limitation of the available water vapor during the condensation process, can be discussed within the framework of the isochoric Köhler equation. To study this effect, we neglect the soot volume and compare systems with different number densities of (equal) droplets and different numbers of H_2SO_4 molecules per droplet. In Figure 6 the classical (solid lines) and isochoric Köhler curves (dotted lines) are plotted for 50 (line a), 10^2 (line b), 10^3 (line c), and 10^4 (line d) H_2SO_4 molecules in the droplet and for different numbers of condensation centers with $N_c = 10^8, \ldots, 10^{15}$ m^{-3}. The corresponding mole fractions of H_2SO_4 in the droplet are shown in Figure 7.

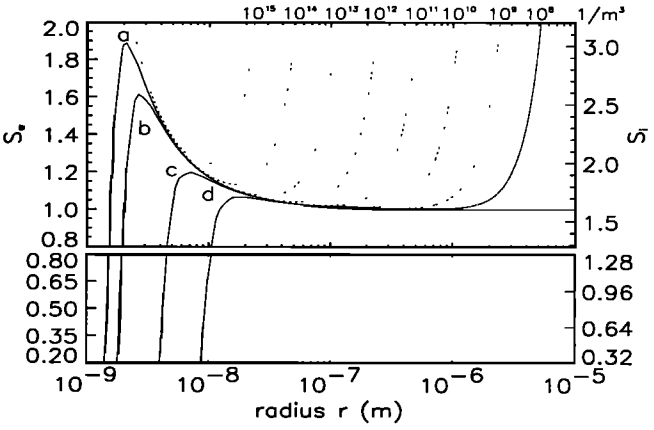

Figure 6. Classical Köhler curves (solid lines) for 50 (line a), 10^2 (line b), 10^3 (line c), and 10^4 (line d) H_2SO_4 molecules together with the corresponding isochoric Köhler curves (dotted) for CN number densities varying between 10^8 and 10^{15} m^{-3}

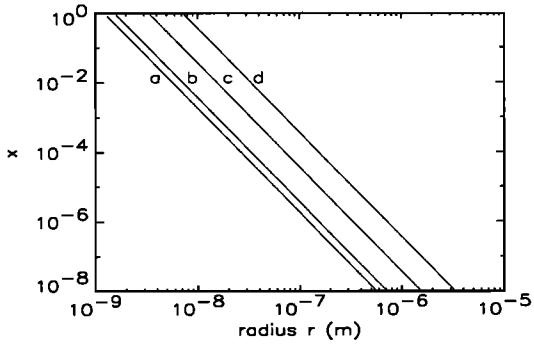

Figure 7. Mole fraction of H_2SO_4 in the droplet versus droplet radius for different amounts of H_2SO_4 molecules: 50 (line a), 10^2 (line b), 10^3 (line c), and 10^4 (line d).

The comparison of the condensation processes leads to the following conclusions: Large numbers of droplets ($> 10^{15}$ m^{-3}) containing small amounts of H_2SO_4 molecules (< 100) can hardly act as effective condensation centers. From the one side the activation of such droplets requires high relative humidities $S_w^{max} > 2$; from the other side, due to the limited amount of water vapor, the maximal radius of such droplets cannot exceed $r \approx 30$ nm (for $S_w^{max} \approx 1.2$). Such droplets (see Figure 7) are strong electrolytes with high mole fractions of H_2SO_4 which, presumably, do not freeze. Consequently, a back transformation from the activated droplets to high concentrated droplets (following the lower arrow in Figure 2) is possible during the plume expansion when the values of S_w drop.

One obtains a completely different picture if the number of condensation centers does not exceed 10^{11} m^{-3} (typical density of soot) and the number of H_2SO_4 molecules per droplet is larger than 1000. According to Figure 7, large droplets with $r \approx 0.5$ μm can be activated for $1 < S_w^{max} < 1.2$ (if heterogeneous corrections are considered, one gets a similar result even for soot particles without H_2SO_4). Such droplets constitute a stable state of the system and can, because of their large dilution, freeze. The formed ice crystals do not evaporate for $S_i > 1$ and may contribute to visible contrails. Consequently, condensation on soot particles seems to be a more favorable process than a homogeneous growth of many small droplets for $S_w^{max} > 1$.

$\mathbf{S_w^{max} < 1}$. Here neither small droplets nor soot particles with or without H_2SO_4 can be activated. A possible stable state of the system consists of small, liquid, droplets with $r \approx 10$ nm which, if they freeze, may grow for $S_i > 1$. According to the equilibrium theory presented, there is no difference in view of condensation processes between soot particles (eventually containing sulfuric acid) and the pure H_2SO_4/H_2O droplets.

5. Conclusions

An extension of the classical Köhler equation to systems with a limited water amount was presented. Compared with the classical approach, such constraint leads to an additional stable state of a liquid droplet containing soluble substance. According to this theory, the effect of hysteresis for droplet growth and shrinkage due to changing relative humidity S_w can be qualitatively described.

The theory was applied for a study of possible condensation processes in aircraft contrails. In particular, we compared three different kinds of water condensation centers: soot, soot covered with sulfuric acid, and pure H_2O/H_2SO_4 droplets. All kinds of particles are released by the aircraft engines and compete during their growth for the water vapor. Here we discussed conditions under which different condensation centers can be activated (in Köhler sense) by taking into account that only a limited amount of water vapor is available during the condensation process.

In particular, a comparison of possible effective droplets radii, their number densities, and the necessary supersaturations for their activation leads to the result that for atmospheric situations where the plume becomes supersaturated with respect to water, a rapid droplet growth on soot particles with or without sulfuric acid followed by subsequently freezing is more favorable than a homogeneous growth of H_2O/H_2SO_4 droplets without soot. According to our discussion there are two reasons for this effect. First, the heterogeneous condensation on soot containing sulfuric acid can occur at much lower supersaturation values than condensation on pure H_2O/H_2SO_4 droplets. Second, the presented discussion of droplets growth in terms of the isochoric Köhler equation leads to activated, i.e., sufficiently large droplets, only if the number of condensation centers does not exceed a critical value defined by the amount of available water vapor. If the plume is undersaturated with respect to water nonactivated and high concentrated H_2O/H_2SO_4 droplets with $r \approx 10$ nm are energetically stable. Furthermore, in view to the water condensation processes, there is no difference between the droplets with and without soot.

It should be emphasized that the presented theory assumes a monodisperse spectrum of condensation centers and consequently neglects different growth processes caused by distinguish initial sizes of the aerosol particles. The measurements of Brock et al. reported by *Fahey et al.* [1995] indicate that large sulfate aerosols (> 100 nm) can successfully compete with soot particles during contrail formation. Furthermore, it is important to note that the analysis of contact angle does not address the issue how soot particles containing sulfuric acid are formed. Here, we explored only the role of the contact angle on the activation of heterogeneous condensation centers, especially on the activation of soot coated with sulfuric acid. We also did not consider the effect of sulfuric acid on the surface properties of soot, but we took into account only the solution effect of sulfuric acid on the heterogenous condensation of water vapor.

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