



BINARY CONDENSATION ON SOLUBLE AEROSOLS—ON THE ACTIVATION AND GROWTH OF THE STRATOSPHERIC AEROSOL FROM COUPLED HNO_3 – H_2O UPTAKE

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Abstract—Combining the well-known binary nucleation theory with the Köhler approach, an equilibrium condensation theory is formulated to study binary condensation processes on soluble aerosols. Especially, an appropriate Gibbs free energy together with the corresponding Kelvin equations are derived. In the case of an ideal droplet (Raoult's law for the activities), the differences between the binary condensation, binary nucleation and the Köhler theory are investigated showing that a stable droplet's state can be predicted only within the framework of the condensation theories. The Gibbs free energy is applied to study the conditions under which stratospheric aerosol particles consisting of liquid sulfuric acid can be activated by coupled HNO_3 – H_2O uptake (binary condensation). Supplementary to the recently published results, an energetic description of the relevant processes is given. In particular, the valley and the minima of the corresponding Gibbs free energy determine the possible condensation processes and the equilibrium states of an aqueous H_2SO_4 – HNO_3 – H_2O droplet. The influence of the Kelvin effect on the critical temperature of activation and on the droplet's composition in the activated state is expected only for the nucleation mode of the stratospheric aerosol, i.e. for sulfuric acid droplets smaller than 10 nm in diameter and with less than 1000 H_2SO_4 molecules per droplet. The critical temperature may fall below the frost point and the HNO_3 percentage of the activated droplets with less than 100 H_2SO_4 particles per droplet is limited by about 40 wt% if the size-independent composition regime ($r > 50$ nm) is reached during the condensation. For H_2SO_4 – H_2O droplets larger than 10 nm this limitation value amounts to about 50 wt% for $r > 100$ nm. In this case, the critical temperature is size-independent.
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1. INTRODUCTION

Generally, aerosol formation with subsequent growth can be considered as either a nucleation or a condensation process. In the first case, one concerns the aerosol formation from one (homomolecular) or more (heteromolecular) vapors. The best-known example of this approach is the binary nucleation theory mainly applied to study the formation of the H_2SO_4 – H_2O droplets (Reiss, 1950; Mirabel and Katz 1974). In the other case, the growth (or evaporation) of preexisting, soluble or insoluble aerosols by uptake of gas particles is considered. An example is the Köhler theory describing the condensation of water vapor on soluble particles (Köhler 1921a, b, 1949, Pruppacher and Klett 1978).

Another point of view classifies the aerosol formation either as homogeneous or heterogeneous phase transition. The former one describes nucleation or condensation which leads to a homogeneous solution droplet, the latter one denotes the phase transition which takes place on the surface of foreign, solid, and insoluble objects.

An effective way to study how the particular atmospheric compounds may be divided into (passive) condensation centers and (active) parts undergoing condensation processes is to construct suitable time scales after which the considered species evolve toward their local equilibrium state. These quantities can be derived from the collision frequencies of all relevant components which, approximately, are proportional to their partial pressures. The recently discussed (binary) HNO_3 – H_2O gas-phase depletion on aqueous sulfuric acid droplets in the stratosphere leading to the formation of PSCs (type Ib) may give an example of a system where binary condensation occurs (Dye *et al.*, 1992; Carslaw *et al.*, 1994; MacKenzie *et al.*, 1995; Meilinger *et al.*, 1995). Here, for low temperatures, the supercooled and high concentrated aqueous H_2SO_4 droplets (passive component) act as effective condensation centers for coupled HNO_3 – H_2O uptake (active species).

Both nucleation and condensation on sufficiently small particles are influenced by the surface tension (Kelvin effect). To take this effect into account, the concept of the Gibbs free energy ΔG can be used that permits to determine the stable and metastable equilibrium states of an isolated aerosol particle together with the Kelvin (energy) barrier ΔG_b , separating these states. This barrier can be overcome for sufficiently high relative partial pressures of the active vapors leading to the so-called activated droplet, i.e., to an energetically unstable aerosol. The further growth of such particle is limited solely by diffusion and the amount of the available condensates.

If only condensation processes are investigated, kinetic models based on the Kelvin (or Gibbs–Thomson) equations are usually used forming a theoretical framework within the dynamic properties of these processes have been successfully studied (Kulmala *et al.*, 1992a, b; Lamb, 1992; Kulmala *et al.*, 1993). However, if additionally the stability of the different equilibrium states or the nucleation rates should be determined, information on the energy barriers ΔG is necessary. Up to this day a complete thermodynamic description (i.e. based on the study of the thermodynamical potential and not only on the use of Kelvin equations) exists for heteromolecular nucleation (Reiss, 1950; Mirabel and Katz, 1974) and for condensation processes of only one component (Köhler theory, Reiss and Koper, 1995). On the other hand, if one is interested in multicomponent condensation processes (as in the case of the coupled HNO_3 – H_2O uptake on aqueous sulfuric acid droplets) an appropriate extension of the well-known theories is desirable.

The aim of this paper is twofold. Firstly, based on the formulations presented by Kulmala *et al.* (1992a, b, 1993), Lamb (1992), and Reiss and Koper (1995), we combine the binary nucleation and Köhler theories to a binary condensation theory on soluble particles. We address this issue in the following section where, in contrast to the formulation presented by Lamb (1992), we not only discuss the appropriate (generalized) Kelvin equations describing the equilibrium state of a ternary droplet in an environment containing two active vapors but, additionally, give a complete formulation of binary condensation in terms of the Gibbs free energy ΔG . In the case of an ideal system, we use this formulation to study the differences between the binary condensation, binary nucleation and condensation of only one component (Köhler theory) and generalize therefore the discussion of stability given by Reiss and Koper (1995) to ternary systems.

Secondly, the presented formulation of the binary condensation is applied to the recently discussed (binary) HNO_3 – H_2O gas-phase depletion on aqueous sulfuric acid droplets in the stratosphere leading to the formation of PSCs (type Ib) [Dye *et al.* (1992)]. This atmospheric system gives an example where for low temperatures the supercooled and high concentrated aqueous H_2SO_4 droplets act as effective condensation centers for coupled HNO_3 – H_2O uptake, i.e. for binary condensation processes. Supplementary to the thermodynamic models presented by Tabazadeh *et al.* (1994), MacKenzie *et al.* (1995), Carslaw *et al.* (1995), or Meilinger *et al.* (1995), we study the stability of the droplets using the Gibbs free energy ΔG . Besides from an energetic view on the undergoing processes, some new results are derived considering the size-dependent activation of the stratospheric sulfate aerosol (especially of its nucleation mode).

2. BINARY CONDENSATION THEORY

2.1. General formulation

Consider a ternary solution droplet with temperature T , surrounded by a gaseous mixture (g) of two active vapors (e.g. an acid and water) with partial pressures p_1^g , p_2^g . Apart from the mol numbers n_1 , n_2 of the active components in the droplet, which are assumed to be in equilibrium with the vapor phase, the solution consists of n_0 mols of an additional soluble aerosol salt or acid (passive component).

Now, we discuss binary condensation of active vapors on the solution droplet under isothermal ($T = \text{const}$) and isobaric ($p_i^g = \text{const}$, $i = 1, 2$) conditions (Fig. 1). In particular, the following two states are considered: The initial (reference) state solely consists of a pure

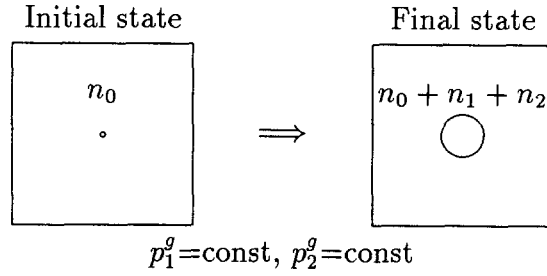


Fig. 1. Definition of the used notation where n_0 is the mol number of the passive component and n_1, n_2 denote the mol numbers of the active condensates in the droplet.

passive aerosol with the mol number n_0 . In the final equilibrium state, the droplet's composition amounts to $n_i, i = 0, 1, 2$, where n_1 and n_2 represent the mol numbers of active vapors which were transferred from the vapor phase to the solution droplet.

To describe phase equilibria, the change of the Gibbs free energy ΔG between the described two states is considered. Separating the bulk and surface contributions, we obtain for a spherical droplet

$$\Delta G = n_0(\mu_0^s - \mu_0^p) + \sum_{i=1}^2 n_i(\mu_i^s - \mu_i^g) + 4\pi r^2 \sigma. \quad (1)$$

Here $\mu_i^s, i = 0, 1, 2$ and $\mu_i^g, i = 1, 2$ are the bulk chemical potentials of the passive and active components in the solution (s) and of active vapors in the gas mixture (g), respectively. Furthermore, μ_0^p is the chemical potential of the passive salt in a pure state (p) and r, σ denote the radius and the surface tension of the droplet, respectively. In the vapor phase the ideal gas equation is valid and the molar volume of the liquid phase is neglected compared with the gaseous state.

The chemical potentials $\mu_i^s, i = 0, 1, 2$ can be related to the corresponding chemical potentials μ_i^p of the pure substances by using the activities a_i , i.e.

$$\mu_i^s = \mu_i^p + RT \ln a_i \quad a_i = \frac{p_i^s}{p_i^p}, \quad (2)$$

where p_i^s and $p_i^p, i = 0, 1, 2$ are the equilibrium pressures of passive and active vapors over a flat surface of the solution and over a flat (liquid or solid) pure substance, respectively. Furthermore, R denotes the universal gas constant.

For a spherical droplet, the radius r satisfies the following relation

$$\frac{4\pi}{3} r^3 \rho = \sum_{i=0}^2 n_i M_i, \quad (3)$$

where ρ is the density of the solution and $M_i, i = 0, 1, 2$ are the molar masses of the particular components. Additionally, we assume that the dependence of σ , and ρ on n_i is given through

$$\sigma = \sigma(x_0, x_1), \quad \rho = \rho(x_0, x_1), \quad (4)$$

where the mass fractions x_i are defined by

$$x_i := \frac{M_i n_i}{\sum_{j=0}^2 M_j n_j}, \quad i = 0, 1. \quad (5)$$

As shown in appendix, equation (1) can be rewritten in the following form:

$$\frac{\Delta G}{RT} = - \sum_{i=1}^2 n_i \ln S_i + \sum_{i=0}^2 n_i \ln a_i + \frac{4\pi r^2 \sigma}{RT} \quad (6)$$

with

$$S_i := \frac{p_i^g}{p_i^p}, \quad i = 1, 2. \quad (7)$$

Here S_1, S_2 denote the relative partial pressures of the active vapors, respectively. Furthermore (see appendix), the activities $a_i, i = 0, 1, 2$ are not independent from each other because the Gibbs–Duhem relations have to be fulfilled, i.e.

$$\sum_{j=0}^2 n_j \frac{\partial \ln a_j}{\partial n_i} = 0, \quad i = 1, 2. \quad (8)$$

Assuming that, similar to σ and ρ , the activities a_i depend on n_i only through the mass fractions x_0 and x_1 , equations (8) can be transformed to

$$\sum_{j=0}^2 \frac{x_j}{M_j} \left((\delta_{0i} - x_i) \frac{\partial \ln a_j}{\partial x_0} + (\delta_{1i} - x_i) \frac{\partial \ln a_j}{\partial x_1} \right) = 0, \quad i = 1, 2. \quad (9)$$

Summarized, the Gibbs free energy can be written as

$$\Delta G = \Delta G(n_1, n_2), \quad (10)$$

where only n_1 and n_2 are the free variables of the considered system. Then, the stable and metastable equilibrium states of the droplet are determined from

$$\frac{\partial \Delta G}{\partial n_1} = 0 \quad \frac{\partial \Delta G}{\partial n_2} = 0, \quad (11)$$

where ΔG is given by equation (6) and, additionally, the relations (3) and (8) (or (9)) have to be fulfilled. Consequently (see appendix), the so-called generalized Kelvin equations

$$\ln \frac{S_i}{a_i} = \frac{2M_i \sigma}{RT r \rho} (1 + \rho^{-1} D[\rho]), \quad i = 1, 2 \quad (12)$$

constitute the necessary conditions for the existence of the extrema of ΔG where the operator D is defined by

$$D = \sum_{j=0}^1 \frac{M_j}{M_i} (\delta_{ij} - x_j) \frac{\partial}{\partial x_j}. \quad (13)$$

Note that although the relations (12) formally agree with the generalized Kelvin equations of the binary nucleation theory (Nair and Vohra 1975; Yue 1979; Yue and Hamill, 1979), the corresponding Gibbs free energy (6) deviates by the term $n_0 a_0$. In addition, if one of the active components is neglected ($n_2 = 0$) then equation (12) with $i = 1$ reduces for $\sigma = \text{const}$ and $\rho = \text{const}$ to the well-known Köhler equation (see e.g. Byers, 1978; Pruppacher and Klett, 1978).

2.2. Binary condensation on an ideal droplet

To show how the binary condensation theory differs from the well-known binary nucleation or the Köhler theory, we consider a simplified system consisting of a liquid droplet with 3 completely soluble and nondissociable components: a passive salt (index 0) and two active condensates (indices 1, 2) in equilibrium with corresponding vapors. The mol numbers and the numbers of molecules in the droplet correspond to n_i and $N_i = N_A n_i$, $i = 0, 1, 2$, respectively, where N_A is the Avogadro number. Although we assume that all components have the same molar masses M , they are considered as distinguishable species. The density ρ and the surface tension σ are constant. Then, by taking into account

equation (3), equations (6) and (12) simplify to

$$\frac{\Delta G}{RT} = - \sum_{i=1}^2 n_i \ln S_i + \sum_{i=0}^2 n_i \ln a_i + \alpha^2 n_t^{2/3}, \quad (14)$$

$$\ln \frac{S_i}{a_i} = \frac{2}{3} \alpha^2 n_t^{-1/3}, \quad i = 1, 2 \quad (15)$$

with

$$n_t = \sum_{i=0}^2 n_i, \quad \alpha^2 = (4\pi)^{1/3} \frac{\sigma}{RT} \left(\frac{3M}{\rho} \right)^{2/3}. \quad (16)$$

Moreover, we assume an ideal behavior of all components in the liquid droplet, i.e. the activities a_i can be described in terms of the Raoult's law:

$$a_i = \frac{n_i}{n_0 + n_1 + n_2}, \quad i = 0, 1, 2. \quad (17)$$

Consequently, the Kelvin equations (15), from which the possible (stable and unstable) equilibrium compositions n_1 , n_2 of the droplet can be calculated, reduce to one equation for n_1

$$\ln S_{\text{tot}} + \ln \left(1 + \frac{n_0}{(1+k)n_1} \right) = \frac{2}{3} \alpha^2 [n_0 + n_1(1+k)]^{-1/3} \quad (18)$$

with $n_2 = kn_1$ and

$$S^{\text{tot}} = S_1 + S_2 = \frac{p_1^g + p_2^g}{p^p} \quad k = \frac{S_2}{S_1} = \frac{p_2^g}{p_1^g}. \quad (19)$$

Here, S_{tot} describes the (total) relative partial pressure of the active vapors. Using equations (14) and (18) we now discuss how the formulated binary condensation theory reduces to the binary nucleation or the Köhler theory.

(1) *Binary nucleation* ($n_0 = 0$). Here, only one unstable equilibrium state of the droplet exists for $S^{\text{tot}} > 1$ (saddle point in Fig. 2a). The critical composition and the corresponding energy barrier $\Delta G_b = \Delta G(n_1^{\text{sad}}, n_2^{\text{sad}}) - \Delta G(0, 0)$ are given through

$$n_1^{\text{sad}} = \frac{\beta}{1+k}, \quad n_2^{\text{sad}} = \frac{\beta k}{1+k} \quad (20)$$

with

$$\beta^{1/3} = \frac{2\alpha^2}{3 \ln S_{\text{tot}}} \quad (21)$$

and

$$\Delta G_b = \frac{20RT\alpha^6}{27 \ln^2 S_{\text{tot}}}. \quad (22)$$

For $0 < S_{\text{tot}} < 1$ a stable droplet cannot exist.

(2) *Köhler theory* ($n_2 = 0$). For diluted solution ($n_0 \ll n_1$) together with $S = S_1$, $S_2 = 0$, and $n = n_1$, equation (18) reduces to the well-known Köhler equation (see e.g. Pruppacher and Klett, 1978; Reiss and Koper, 1995; Konopka, 1996):

$$\ln S = \frac{2}{3} \alpha^2 n^{-1/3} - \frac{n_0}{n}. \quad (23)$$

For $1 < S < S_c$, ($S_c = \exp \delta$, $\delta = (2/n_0)^{(1/2)} 4\alpha^3/27$), two equilibrium states are possible: a stable droplet with the mol numbers n_0 , n^{min} and an unstable one with the composition n_0 , n^{max} (see Fig. 2). The values of n^{min} and n^{max} can be determined only numerically. The energy barrier ΔG_b amounts to $\Delta G_b := \Delta G(n^{\text{max}}, 0) - \Delta G(n^{\text{min}}, 0)$. For $S < 1$ only a stable droplet with mol numbers n_0 , n^{min} can exist; for $S > S_c$ an activated droplet should be expected.

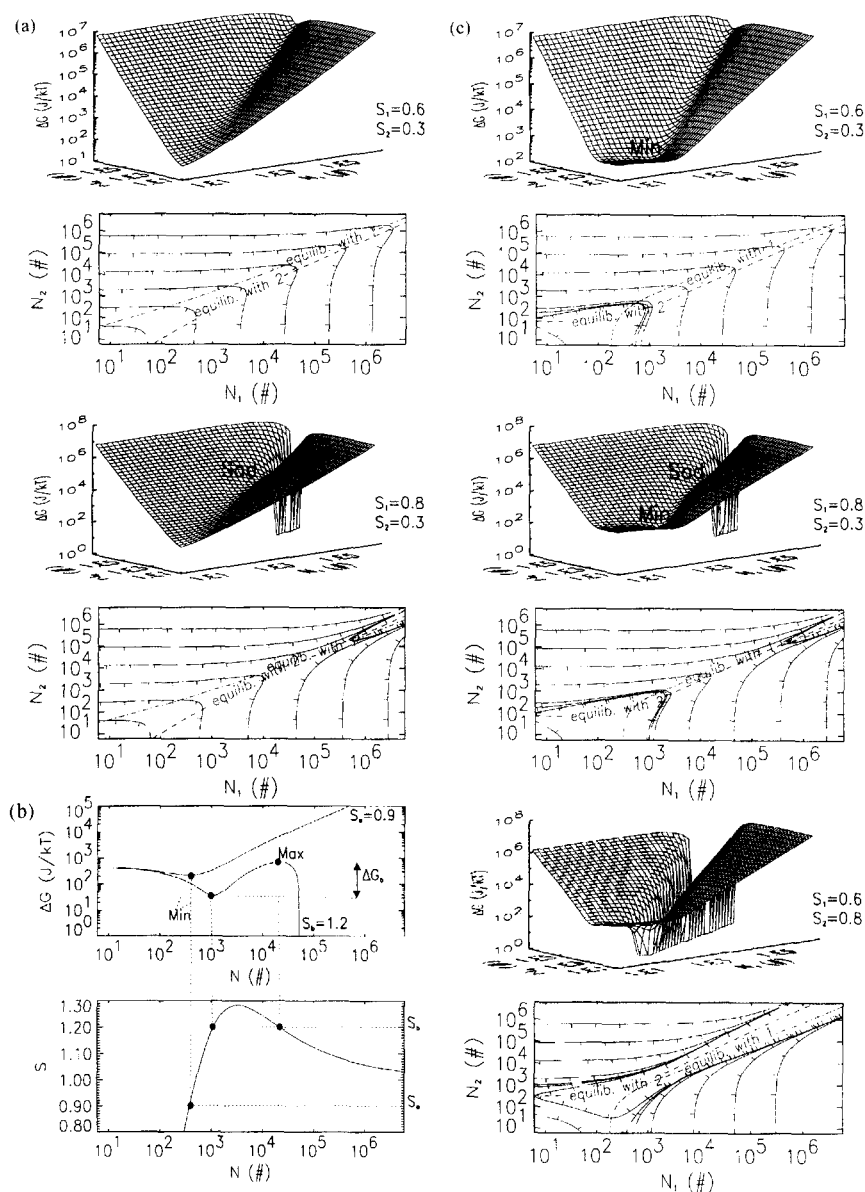


Fig. 2. (a) Binary nucleation, (b) Köhler theory, and (c) binary condensation for an ideal liquid droplet (Min—minimum, Max—maximum, Sad—saddle point, $\alpha = 10^{-7}$). For cases (a) and (c), the Gibbs free energy ΔG in kT units (upper panels), its contour plot together with the Kelvin equilibrium trajectories (lower panels) are shown for different values of $S_{\text{tot}} = S_1 + S_2$. Both, ΔG and its contour plot are plotted versus N_1, N_2 describing the number of active molecules in the droplet. The dashed and dot-dashed Kelvin equilibrium trajectories in the contour plot are derived from equations (18). In case (b), Köhler equation (lower panel), and the corresponding Gibbs free energy in kT units (upper panel) are shown for two values of S . ΔG_b denotes the energy barrier. The number of passive molecules N_0 in the droplet (cases (b) and (c)) amounts to 400. A nucleating or condensing droplet is activated if the energy barrier is overcome during its growth.

The possible behaviors during the binary condensation are shown in Fig. 2c. In addition to the (unstable) saddle point, the minimum describes a stable droplet. Similar to the Köhler approach this minimum is a consequence of the entropy increase during the mixing of the salt with the condensing vapors. For diluted solution $n_0 \ll n_1, n_2$, the minimum and the saddle point exist for $0 < S_{\text{tot}} < S_c$ and $1 < S_{\text{tot}} < S_c$, respectively. The energy barrier between the minimum and the saddle point vanishes for $S_{\text{tot}} > S_c$.

Summarized, a droplet is activated if for sufficiently large values of S_{tot} the droplet's size has overcome the critical composition connected with the unstable equilibrium state. It should be emphasized that in the case of binary nucleation or binary condensation, supersaturation of the active components (with respect to their pure states) is not a necessary condition under which activation may occur. The much weaker condition, $S_{\text{tot}} > 1$, guarantees the existence of a saddle point, even if nonideality of the solution is neglected. Furthermore, the stable states of a droplet are possible only within the condensation theories.

3. $\text{H}_2\text{SO}_4\text{--HNO}_3\text{--H}_2\text{O}$ TERNARY DROPLETS IN THE STRATOSPHERE

Based on the study of the equilibrium vapor pressures over a (bulk) $\text{H}_2\text{SO}_4\text{--HNO}_3\text{--H}_2\text{O}$ system, Kiang and Hamill (1974) firstly reported the possibility that stratospheric aqueous H_2SO_4 aerosols may significantly absorb nitric acid. Recent laboratory measurements (Zhang *et al.*, 1993) and model calculations (Luo *et al.*, 1995) also suggest that HNO_3 is highly soluble in aqueous H_2SO_4 solutions at low temperatures. Especially, thermodynamic equilibrium models of bulk properties show that aqueous H_2SO_4 under stratospheric conditions absorbs large amount of HNO_3 and H_2O from the gas phase for temperatures below the nitric acid trihydrate (NAT) saturation temperature and above the ice frost point (Tabazadeh *et al.*, 1994; Carslaw *et al.*, 1994; MacKenzie *et al.*, 1995; Meilinger *et al.*, 1995). The calculated change in the total volume of the aerosol (Carslaw *et al.*, 1994) was shown to agree closely with *in situ* observations made in the Arctic during the winter of 1989 (Dye *et al.*, 1992). The mentioned theoretical studies assume that high concentrated H_2SO_4 aerosols can be considered as aqueous condensation centers on which the binary $\text{HNO}_3\text{--H}_2\text{O}$ condensation occurs.

The aim of this section is to apply the presented binary condensation theory to the $\text{H}_2\text{SO}_4\text{--HNO}_3\text{--H}_2\text{O}$ system under stratospheric conditions and to study, supplementary to the mentioned theoretical studies, both the stability and the activation of the sulfuric aerosol during the $\text{HNO}_3\text{--H}_2\text{O}$ uptake.

3.1. Input parameters

In the following, we use the notation: H_2SO_4 —index 0, HNO_3 —index 1, H_2O —index 2. The temperature-dependent surface tension σ and the density ρ of the considered ternary system are obtained from the experimental data of the binary $\text{H}_2\text{SO}_4\text{--H}_2\text{O}$ and $\text{HNO}_3\text{--H}_2\text{O}$ systems (Resch, 1995; Beyer *et al.*, 1996) and by using the mol-weighted composition rule (Carslaw 1994):

$$f(x_0, x_1) = \frac{M_1 x_0}{M_1 x_0 + M_0 x_1} f_0(x_0) + \frac{M_0 x_1}{M_1 x_0 + M_0 x_1} f_1(x_1) \quad (24)$$

with $f \in \{\sigma, \rho\}$ (Fig. 3).

The acid and water activities a_1, a_2 are calculated from

$$a_1(x_0, x_1) = \frac{p_{\text{HNO}_3}(x_0, x_1)}{p_{\text{HNO}_3}(0, 1)}, \quad (25)$$

$$a_2(x_0, x_1) = \frac{p_{\text{H}_2\text{O}}(x_0, x_1)}{p_{\text{H}_2\text{O}}(0, 0)}$$

where the partial pressures $p_{\text{HNO}_3}, p_{\text{H}_2\text{O}}$ of the $\text{H}_2\text{SO}_4\text{--HNO}_3\text{--H}_2\text{O}$ solution for $185 \leq T \leq 235$ and $0 \leq x_0 + x_1 \leq 0.7$ were recently published (Luo *et al.*, 1995). Note, that the choice of the reference pressures do not influence neither the possible equilibrium states of the droplet (equation (12)) nor the Gibbs free energy ΔG (equation (6)) nor the Gibbs–Duhem relation (equation (8)), if the same reference pressures are used in the definitions of S_1 and S_2 . Furthermore, as a consequence of the Gibbs–Duhem relations (9),

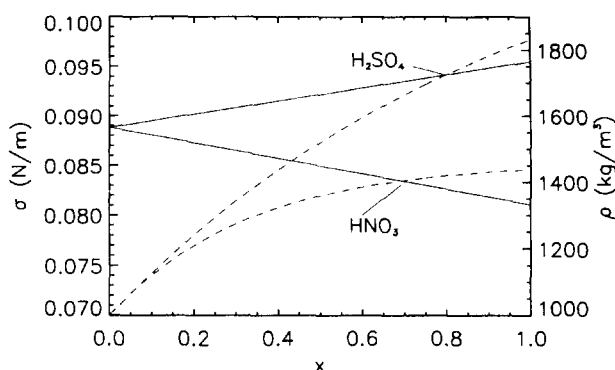


Fig. 3. Surface tension σ (solid lines) and density ρ (dashed lines) for the binary H_2SO_4 - H_2O and HNO_3 - H_2O solutions versus weight fraction x at $T = 191$ K (Resch, 1995).

the activities a_1 , a_2 fulfill the following equation:

$$\frac{\partial \hat{A}(x_0, x_1)}{\partial x_0} - \frac{\partial \hat{B}(x_0, x_1)}{\partial x_1} = 0 \quad (26)$$

with

$$\hat{A} = x_1(A_2 - A_1), \quad \hat{B} = A_2 - \hat{A} \quad (27)$$

and

$$A_i = -\frac{M_0}{x_0} \sum_{j=1}^2 \frac{x_j}{M_j} \left(\frac{\partial \ln a_j}{\partial x_0} + k_i \frac{\partial \ln a_j}{\partial x_1} \right), \quad (28)$$

$$k_1 = \frac{x_1 - 1}{x_1}, \quad k_2 = 1, \quad i = 1, 2.$$

It can be shown that, although equation (26) is valid for an ideal ternary system satisfying the Raoult's law, this relation is partially violated for the activities a_1 , a_2 calculated from Luo *et al.* (1995). Especially, considering the relative residuum r of equation (26) defined as

$$r = \frac{1}{c} \left(\frac{\partial \hat{A}}{\partial x_0} - \frac{\partial \hat{B}}{\partial x_1} \right), \quad c = \left| \frac{\partial \hat{A}}{\partial x_0} \right| + \left| \frac{\partial \hat{B}}{\partial x_1} \right| \quad (29)$$

for a_1 , a_2 at 191 K, one obtains $\bar{r} = 0.2\%$ and the mean value of $|r - \bar{r}|$ calculated over the whole domain $0 < x_0 + x_1 < 0.7$ amounts to 25% indicating strong fluctuations of r for some values of x_0 and x_1 . Consequently, we do not determine a_0 from the Gibbs–Duhem relations (9), but use the following approximation:

$$a_0(x_0, x_1) = a_0(x_0) = \frac{p_{\text{H}_2\text{SO}_4}(x_0)}{p_{\text{H}_2\text{SO}_4}(1)}, \quad (30)$$

where the parameterization proposed by Resch (1995) with $q = 3.5$ is used (Fig. 4). Note, that a_0 has only a minor importance on the following results due to the fact that equation (12) and, consequently, the possible equilibrium states of the droplet are independent on a_0 . Here, only the values of the energy barriers separating different equilibrium states are influenced by a_0 (equation (6)).

3.2. Results

By neglecting of the operator D , i.e. by neglecting the derivatives of ρ with respect to x_0 and x_1 due to a negligible dependence of ρ on the composition, we apply equations (6) and (12) and discuss the binary HNO_3 - H_2O condensation on aqueous H_2SO_4 droplets under the same stratospheric conditions as discussed in Carslaw *et al.* (1994). In particular,

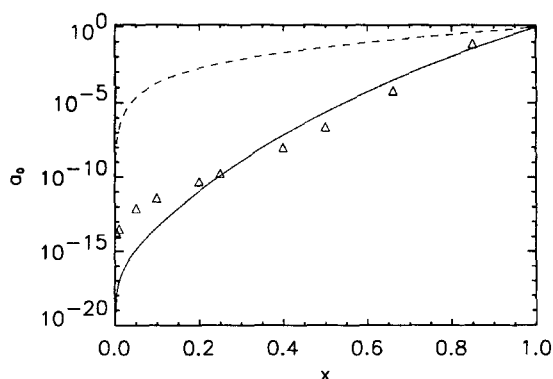


Fig. 4. Activity a_0 of an H_2SO_4 aqueous solution versus weight fraction x at $T = 191$ K by using the parameterization proposed by Resch (1995) with $q = 3.5$ (solid line). For comparison, the ideal approximation (Raoult's law) is also shown (dashed line). The triangles denote the experimental data of Nair and Vohra (1975) for $T = 298.15$.

we assume typical H_2O and HNO_3 concentrations corresponding to 5 ppmv and 10 ppbv, respectively, for an altitude with 55 hPa air pressure.

Firstly, to show how the presented theory works, we consider a droplet containing 5000 H_2SO_4 particles at NAT saturation temperature $T = 196$ K (left side of Fig. 5) and at frost point $T = 189$ K (right side of Fig. 5). Especially, we investigate the Gibbs free energy (6) in the $N_1 - N_2$ space, where N_i , $i = 1, 2$ denote the numbers of HNO_3 and H_2O particles in the droplet, respectively (upper and middle panel in Fig. 5). Additionally, the curves along which the droplet is in equilibrium either with HNO_3 or with H_2O vapor (equations (12) with $i = 1, 2$) are plotted in Fig. 5.

Strictly speaking, only the intersection points between the generalized Kelvin curves (12) are the possibly equilibrium states of the droplet. Similar to our discussion in the previous section and by taking into account the Gibbs free energy (6), these states can be divided into energetically stable and unstable. In addition, the energy barriers separating these states can be determined.

For two reasons, we apply here only a simplified version of such discussion. On the one side, the Gibbs free energy ΔG has a valley defined by the equilibrium curves (12) which show, independent on the temperature, a very similar course. Consequently, at each point of the valley the droplet is in approximate equilibrium with water and acid vapor. The intersection points of such similar Kelvin curves together with ΔG values at these points are strongly sensitive to the experimental data which, according to the discussed assumptions and limitations, are not known with sufficient precision. On the other hand, the concept of the Gibbs free energy assumes a system with constant pressures of the active components ($p_1^e, p_2^e = \text{const}$) and, consequently, only permits to determine the stable state of the non-activated droplet together with the energy barrier separating this state from the region with an unlimited droplet's growth. For systems with a limited amount of available water or acid vapor, the Gibbs free energy has to be replaced by the Helmholtz free energy (Konopka and Vogelsberger, 1996).

Furthermore, we assume that the valley of ΔG defined by the Kelvin equations (12) constitutes the possible trajectories of HNO_3 - H_2O condensation on a H_2SO_4 - H_2O droplet. The possible stable states of the droplet are determined by the absolute minimum of the valley (denoted by E in Fig. 5). For sufficiently high temperatures, the valley starts at the stable equilibrium characterized by a pure H_2SO_4 - H_2O droplet (here at $T = 196$). Then, if the temperature decreases, a new minimum of the valley arises (here at $T = 189$). This state describes an activated, unstable droplet mainly consisting of a HNO_3 - H_2O solution. The growth of such a droplet is limited only by diffusion. During the cooling with temperatures between 196 and 189 K, we assume that the activation occurs if at least along one of the (Kelvin-) trajectories ΔG monotonically decreases. The corresponding temperature denotes the critical temperature T_c .

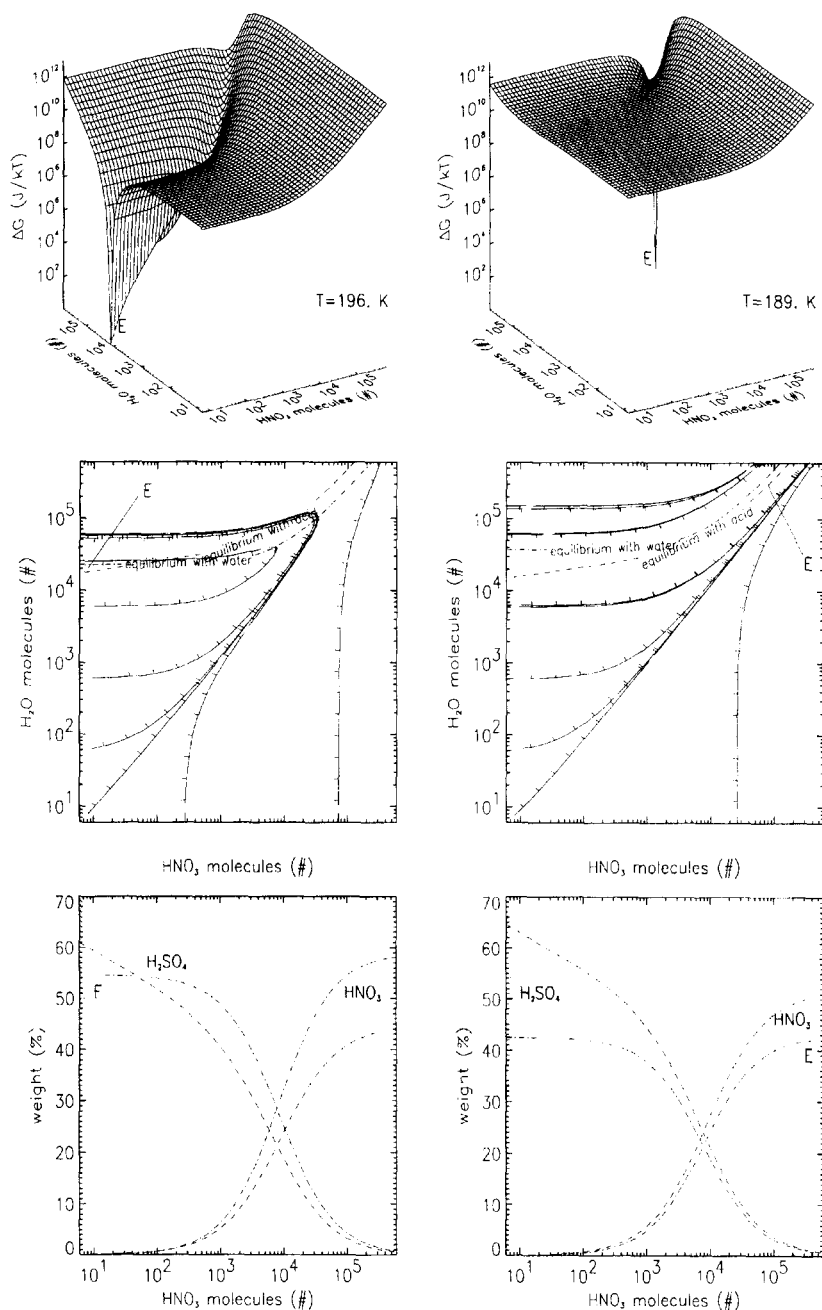


Fig. 5. Gibbs free energy ΔG (upper panels), its contour plot together with the Kelvin equilibrium trajectories (middle panels), and droplet's composition along these curves (lower panels) for a sulfuric acid droplet containing 5000 H_2SO_4 particles at NAT saturation temperature $T = 196$ K (left side) and at ice frost point $T = 189$ K (right side). Both, ΔG and its contour plot are shown versus N_1, N_2 describing the number of HNO_3 and H_2O molecules in the droplet, respectively. ΔG , plotted in kT units, is shifted in such a way that its minimum E corresponds to $\Delta G/kT = 1$. The dashed and dot-dashed Kelvin equilibrium trajectories in the contour plot are derived from equations (12) with $i = 1, 2$ and describe the equilibrium states with respect to acid and water, respectively. The weight percentages of H_2SO_4 and HNO_3 in the droplet are calculated along the corresponding Kelvin equilibrium trajectories.

Now, we investigate the dependence of T_c on the H_2SO_4 content in the droplet (Fig. 6). We see that at 55 hPa altitude with $15 \leq [\text{HNO}_3] \leq 5$ ppbv and $\text{H}_2\text{O} = 5$ ppmv, the activation of small H_2SO_4 - H_2O droplets ($r < 5$ nm) containing less than 10^3 H_2SO_4 molecules may firstly occur at temperatures below the frost point. Furthermore, in

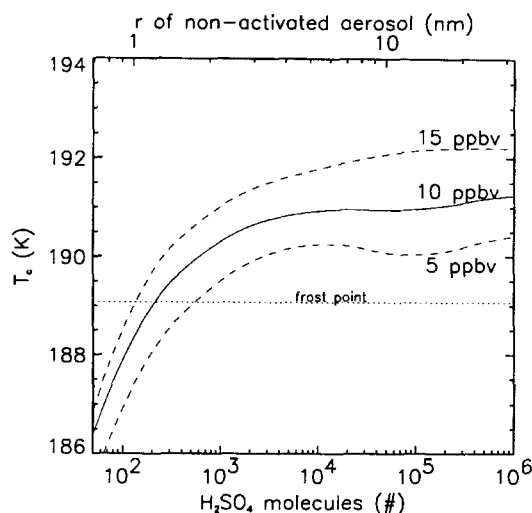


Fig. 6. Critical temperatures T_c versus H_2SO_4 content in the droplet (or its corresponding radius in the non-activated state) for 55 hPa altitude, 5 ppmv H_2O , and 10 ppbv HNO_3 (solid line). The dashed lines describe the cases with 5 and 15 ppbv HNO_3 , respectively. The dotted line denotes the ice saturation, the NAT saturation temperature amounts to 196.2 K (Carslaw *et al.*, 1994).

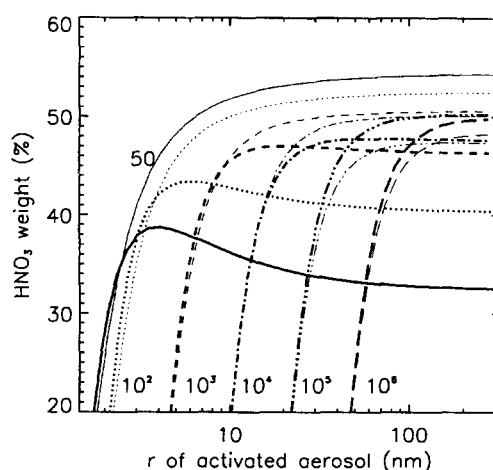


Fig. 7. Droplet's weight percentage of HNO_3 versus droplet's radius for different H_2SO_4 amounts in the droplet along two different condensations paths. The solid, dotted, dashed, dot-dashed, triple-dot-dashed and long-dashed lines correspond to 50, 10^2 , 10^3 , 10^4 , 10^5 , and 10^6 H_2SO_4 molecules in the droplet. Condensation along the bold lines is more favorable.

accordance with the prediction of Carslaw *et al.* (1994), T_c increases with increasing HNO_3 content in the atmosphere.

Another interesting point is the droplet composition with respect to HNO_3 along the Kelvin equilibrium curves at temperature $T = T_c$ and for different initial H_2SO_4 amounts N_0 in the droplet (Fig. 7). Here, the HNO_3 weight percentages in the droplet versus droplet's radius are shown for N_0 varying between 50 (solid lines) and 10^6 (long dashed lines) H_2SO_4 particles in the droplet. The upper and lower curves correspond to the weight percentages of HNO_3 calculated along Kelvin curves (12) describing an equilibrium with respect to HNO_3 ($i = 1$) and H_2O ($i = 2$), respectively. The bold line denotes the more favorable paths. In particular, for droplets with less (more) than 10^5 H_2SO_4 molecules one obtains, that equilibrium condensation with respect to H_2O (HNO_3) should be expected. Furthermore, the droplet's composition with respect to HNO_3 reaches approximately a constant value for

radii larger than a certain critical value r_c depending on the H_2SO_4 amount in the droplet. The HNO_3 content of activated droplets (in wt%) varies between 32 and 47% (47 and 50%) for $50 < N_0 < 10^3$ ($10^3 < N_0 < 10^6$) and $r_c > 10$ nm (100 nm).

4. DISCUSSION AND CONCLUSIONS

An equilibrium theory describing binary condensation theory on soluble aerosols was considered. The presented formulation, which combines the binary nucleation theory and Köhler's approach, consists of an appropriate Gibbs free energy (6) and the generalized Kelvin equations (12). Using these equations, the possible equilibrium states together with the corresponding energy barriers of a (ternary) droplet solution undergoing condensation in a binary vapor can be derived. Of course, following the methods developed in this paper, the theory can be easily rewritten for a droplet containing n soluble species and taking up m ($m < n$) gaseous components.

It should be noted that a condensation theory removes an important shortcoming of the formally very similar binary nucleation theory. In contrast to the latter one, the existence of a macroscopic condensation center guarantees that at each stage of the condensation process itself, the droplet retains its macroscopic properties and, consequently, the bulk description can be used. On the other side, the nucleation embryos predicted in terms of the binary nucleation theory consists of only few molecules (see e.g. Hamill *et al.*, 1976; Hidy *et al.*, 1978). The properties of such microscopic droplets may significantly differ from the used bulk data yielding a contradiction to the macroscopic formulation of this theory.

Based on the presented formulation, the differences between the binary and singular condensation as well as between condensation and nucleation itself were discussed for an ideal system. It could be shown that nonideality does not force additional new behaviors of the system. All well-known properties (stable states, energy barriers) have to be expected in the ideal case.

The theory was applied to the recently discussed H_2SO_4 – HNO_3 – H_2O ternary system in the stratosphere. Based on the activities published by Luo *et al.* (1995), the binary HNO_3 – H_2O condensation on aqueous H_2SO_4 droplets for low temperatures was investigated. Supplementary to the theoretical approach presented in Dye *et al.* (1992), Carslaw *et al.* (1994), MacKenzie *et al.* (1995), and Meilinger *et al.* (1995), the stability and activation of the stratospheric sulfur aerosol were investigated, leading to the following results:

1. A strong uptake of HNO_3 for temperatures below NAT saturation temperature and above ice frost point could be confirmed only for aqueous H_2SO_4 droplets larger than 10 nm in diameter and with more than 1000 H_2SO_4 particles per droplet.

2. Such droplets are activated (i.e. unstable) below the critical temperature T_c that is approximately independent on droplet's radius. The following condensation is limited only by diffusion, i.e. by the available amount of HNO_3 and H_2O vapors. For sufficiently large droplets ($r > 100$ nm) the size-independent HNO_3 percentage weight of about 48 wt% is reached.

3. The critical temperature T_c of non-activated H_2SO_4 – H_2O droplets smaller than 10 nm in diameter (i.e. with less than 1000 H_2SO_4 particles per droplet) falls with decreasing droplet's size. For sufficiently small droplets, the activation may firstly occur below the frost point.

4. The HNO_3 uptake processes on such droplets are less effective than on H_2SO_4 droplets with diameters exceeding 10 nm. In the size-independent composition range, the percentage weight of HNO_3 is less than 40 wt% for droplets containing less than 100 H_2SO_4 particles.

The fact that aqueous H_2SO_4 droplets with a diameter $d > 10$ nm can be activated by higher temperatures than droplets with $d < 10$ nm may, give a further hint for the bimodal structure of the stratospheric aerosol: In the statistical sense, stratospheric conditions with temperatures below the frost point are more exceptional than temperatures exceeding this

point. Consequently, it is more likely to activate a H_2SO_4 droplet with $d > 10$ than a droplet below this critical size leading to the accumulation of droplets in a mode with $d < 10$ nm. Furthermore, activated droplets undergo condensation processes connected with an effective uptake of HNO_3 – H_2O . Due to the limitation of the available HNO_3 and H_2O amount, the resulting droplets can be accumulated in the second mode existing between 0.1 and 1 μm .

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APPENDIX: DERIVATIONS OF THE EQUATIONS (6), (8), (9) AND (12)

Firstly, we prove the relation (6). Using of the equilibrium relation

$$\left(\frac{\partial \mu}{\partial p}\right)_T = v, \quad (\text{A1})$$

where v is the molar volume of the considered substance, we determine the difference of the chemical potentials μ^p and μ^g of the pure (liquid) and gaseous phases, respectively. Due to the assumption $v^p \ll v^g$, we obtain

$$\frac{\partial}{\partial p}(\mu^p - \mu^g) = v^p - v^g \approx -v^g = -\frac{RT}{p}, \quad (\text{A2})$$

where the ideal gas equation was used for the gaseous state. Considering an isothermal process between a state characterized by $p = p_1$, $\mu^p = \mu^g$ and an arbitrary state with $p = p_2$ yields

$$\mu^p - \mu^g = -RT \int_{p_1}^{p_2} \frac{1}{p} dp = -RT \ln \frac{p_2}{p_1}. \quad (\text{A3})$$

Now, the differences of the chemical potentials in equation (1) can be determined, i.e.

$$\mu_0^s - \mu_0^g = RT \ln a_0, \quad (\text{A4})$$

$$\mu_i^s - \mu_i^g = -RT \ln \frac{p_i^g}{p_i^s} = -RT \ln \frac{S_i}{a_i} \quad (\text{A5})$$

with $i = 1, 2$. Inserting these relations into (1) leads to equation (6).

Due to the fact that μ_i^s , $i = 0, 1, 2$ are the bulk chemical potentials of the solution, the Gibbs free energy G_s of a bulk solution consisting of a constant mol number of aerosol salt n_0 and variable mol numbers n_1, n_2 can be written as

$$G_s(n_1, n_2) = \sum_{i=0}^2 n_i \mu_i^s(n_1, n_2) \quad (\text{A6})$$

where the right-hand sides of the above equations are a consequence of the homogeneity of G_s , i.e.

$$G_s(\lambda n_1, \lambda n_2) = \lambda G_s(n_1, n_2), \quad \forall \lambda \in \mathbb{R}^+. \quad (\text{A7})$$

Then, differentiation of G_s with respect to n_i leads to

$$\frac{\partial G_s}{\partial n_i} = \mu_i^s + \sum_{i=0}^2 n_i \frac{\partial \mu_i^s}{\partial n_i} = \mu_i^s, \quad i = 1, 2. \quad (\text{A8})$$

Consequently, taking equation (2) into account, one obtains equation (8). Additionally, with

$$\frac{\partial x_i}{\partial n_j} = \frac{x_i}{n_j} (\delta_{ij} - x_j), \quad i, j = 0, 1, 2 \quad (\text{A9})$$

a straightforward calculation leads to equation (9).

Differentiation of equation (6) with respect to n_i together with relation (8) leads to

$$\frac{\partial \Delta G}{\partial n_i} = -RT \ln S_i + RT \ln a_i + 8\pi r \sigma \frac{\partial r}{\partial n_i} + 4\pi r^2 \frac{\partial \sigma}{\partial n_i}, \quad i = 1, 2. \quad (\text{A10})$$

To determine the partial derivatives of r , the derivation of (3) with respect to n_i is considered. One obtains

$$\frac{\partial r}{\partial n_i} = \frac{1}{4\pi r^2 \rho} \left(M_i - \frac{4}{3} \pi r^3 \frac{\partial \rho}{\partial n_i} \right). \quad (\text{A11})$$

In addition, according to the chain rule, for an arbitrary function $f = f(x_0, x_1)$ we yield

$$\frac{\partial f}{\partial n_i} = \sum_{j=0}^1 \frac{\partial f}{\partial x_j} \frac{\partial x_j}{\partial n_i}. \quad (\text{A12})$$

Consequently, one can write

$$\frac{\partial \rho}{\partial n_i} = \frac{3M_i}{4\pi r^3 \rho} D[\rho], \quad \frac{\partial \sigma}{\partial n_i} = \frac{3M_i}{4\pi r^3 \rho} D[\sigma] \quad (\text{A13})$$

and

$$\frac{\partial r}{\partial n_i} = \frac{M_i}{4\pi r^2 \rho} (1 - D[\rho]). \quad (\text{A14})$$

After inserting these relations into equation (A10) and assuming that due to the Gibbs adsorption equation the derivatives of σ with respect to the composition should vanish (Wilemski, 1984; Reiss and Koper, 1995), relation (12) can easily be derived.