

## Thermodynamic Modeling of Aerosol Watering in the Atmosphere

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### Abstract

Thermodynamic models of extremal intermediate states (MEIS) are used to describe the features of the formation of nucleating drops and aerosol watering in the atmosphere. Advantages of MEIS in describing phase transitions in multicomponent systems are shown. Results of the calculation of the equilibrium (thermodynamically most probable) drop radius are discussed for different ratios of the soluble to insoluble components of the condensation nuclei. The proposed approach allows numerical investigation of the effect of meteorological conditions on microphysical characteristics of haze, clouds and fog. Theoretical substantiation of size distribution of the aerosol of different origin will allow estimating possible anthropogenic effect on optical characteristics of the atmosphere, which are one of the basic climate-forming factors.

### EFFECTS OF AEROSOL CONDENSATION AND WATERING IN THE ATMOSPHERE

A 4–5-fold supersaturation is theoretically necessary for the nuclei of a new phase (liquid water) to be formed in absolutely clean air (*i. e.*, the air containing no heterogeneous admixtures) [1]. Numerous observations suggest that real supersaturation in atmosphere does not exceed 1 %, since a large number of condensation nuclei (CN) is always present in the air [2].

Heterogeneous condensation of moisture on aerosol particles is determined first of all by the solubility of the substance on particle surface. In the semi-empirical theory of equilibrium condensation enlargement of atmospheric aerosol particles [3], the equilibrium particle radius  $r(f)$  at relative humidity of the air  $f$  is linked with the radius of a dry particle  $r_0$  by the equation:

$$r(f) = r_0 \left[ 1 - \frac{BE_v}{\ln f} \right]^{1/3} \quad (1)$$

where  $B$  is empirical coefficient,  $E_v$  is volume fraction of water-soluble substances in aerosol particles. For troposphere aerosol, an experimental dependence was obtained [4]:

$$E_v = y_0 + A \exp \left[ -0.5 \left( \frac{\ln(r/x)}{w} \right)^2 \right] \quad (2)$$

where  $y_0 = 0$ ,  $A = 0.4$ ,  $x = 0.32 \mu\text{m}$ ,  $w = 0.6$ .

Evolution of aerosol particles in the atmosphere passes through the following stages: 1) formation of condensation nuclei; 2) change of particle size at the changes of relative humidity under the conditions of undersaturation (nucleus watering); 3) ageing of droplet aerosol, accompanied by the change of the fractional distribution of particles; 4) formation of the droplets of clouds and fog under supersaturation conditions.

Aerosol watering is accompanied by the dissolution of a part of the substance of CN and leads to a change of the total refractive index. Optical changes start at the relative humidity of 25–30 %; this fact is used in experimental investigations of atmospheric aerosol. Traditionally, thermodynamic modeling is used to interpret the data of optical observations, which allows one to imitate the total effect of the latter three stages of the process under question at the known composition of condensation nuclei.

Conventional calculations of droplet size distribution are based on using equilibrium con-

stants obtained experimentally for binary and ternary combinations of the dissolved substances. Such an approach is complicated by the competing action of salt effects and surface tension on vapour saturation pressure and thus on droplet size. Real condensation nuclei are composed of tens salts, which leads to substantial decrease in the accuracy of thermodynamic calculations.

#### MODELS OF EXTREME INTERMEDIATE STATES

Unlike the traditional thermodynamic approach, models proposed by the ESI SB RAS allow one to investigate not only the final equilibrium state of a system but also a series of intermediate states attainable in course of its relaxation to the final equilibrium state [5, 6]. Among the developed models of the formation of condensed phase in the atmosphere the most general one takes into account the surface tension, electric charge of droplets, and dissolution of hazardous substances in them in the approximation of diluted solution; the model is as follows:

to find  $\max(F)$

$$F(\mathbf{x}) = \sum_{j \in J} c_j x_j \quad (3)$$

subject to the conditions:

$$\mathbf{Ax} = \mathbf{b} \quad (4)$$

$$D_i(\mathbf{y}) = \{\mathbf{x} : G(\mathbf{x}^{eq}) \leq G(\mathbf{x}) \leq G(\mathbf{y});$$

$$G(\mathbf{x}') \geq G(\mathbf{x}''), x_j \geq 0 \quad (5)$$

where  $\mathbf{x}$  is the vector of the amount of components of the system, mol;  $c_j$  is a coefficient to range the hazardous properties (or other characteristics) of a component  $j$  of vector  $\mathbf{x}$ ,  $c \geq 0$ ;  $\mathbf{y}$  is the vector of the amount of initial reagents, mol;  $G$  is the energy of Gibbs of the system;  $\mathbf{A}$  is a  $(m \times n)$  matrix describing the content of elements in the components of the system;  $\mathbf{b}$  is a vector of the amount of elements, mol;  $\mathbf{x}^{eq}$  is the point of global (final) equilibrium of the system;  $\mathbf{x}'$  and  $\mathbf{x}''$  are points located on thermodynamically admissible trajectories in the space of compositions,  $\mathbf{x}'$  being located earlier than  $\mathbf{x}''$  at the system's trajectory;  $D_i(\mathbf{y})$  is a set (region) of thermodynamic

attainability from the initial state;  $J$  is a set of components included in the consideration.

It should be noted that the authors of the models of extreme intermediate states (MEIS) succeeded in solving the problem of formalized description of phase transitions in multi-component medium. Many researchers use molar fractions of substances as the components of  $x_i$  vector of composition  $\mathbf{x} \in R_+^n$ , disregarding the number of phases in which these substances can be present [7]. For example, if a substance  $A$  is present in three phases (gas, liquid, and solid), it is represented by a single component of the  $\mathbf{x}$  vector. For this approach, thermodynamic functions are assigned in intervals, because they change linearly for the condensed state. In multidimensional cases, a correct assignment of slice functions and origination of several local extreme points cause substantial difficulties in solving the problem of searching for global extremum.

The authors of [6, 8] use the approach describing one and the same substance in different phases by separate components of the composition vector  $\mathbf{x}$ . Increasing the dimensionality of the task and bringing no distortions to the physical sense, they succeeded in getting rid of interval assignment of the functions. It is proved that in case of such a formulation, the tasks in which ideal solutions are taken into account along with gas-phase and condensed substances are convex [5].

Investigation of phase transitions of water in the atmosphere is traditionally based on the assumption that two interacting phases are in stable equilibrium [3]. At the same time, experiments show that all the phase transitions in truly uniform systems (free of solid impurities, charged ions, physical non-uniformities) occur through a metastable state [1]. It is this metastable state in which the nuclei of a new phase (water droplet nuclei) are formed. The metastable state is thermodynamically non-equilibrium (is not a state of the final equilibrium of the system), but it can be conserved for rather long time. An intermediate incomplete equilibrium corresponds to a local extremum of a thermodynamic state function (for example, to a maximum of entropy or minimum of the Gibbs' free energy of the sys-

tem), while the final equilibrium is a global extremum in the space of possible compositions of the given system [6, 7]. The formation of the nucleating water droplets should be considered in the general case as an intermediate equilibrium. At the same time, the objective function of this problem, which is reduced to the search for the minimum of Gibbs' energy ( $G$ ), can be written down as

$$G = \sum_{j \in J_g} \left( G_j^0 + RT \ln \frac{x_j}{\sigma} \right) x_j + \left( G_w^0 + \frac{2\alpha V_c}{r} + \frac{3q^2 V_c}{32\pi^2 r^3} \left( \frac{1}{r} + \frac{1}{\alpha \epsilon} \right) + RT \ln \frac{x_w}{\sigma_s} \right) x_w + \sum_{j \in J_c} G_j^0 x_j + \sum_{j \in J_s} \left( G_j^0 + RT \ln \frac{x_j}{\sigma} \right) x_j \quad (6)$$

where

$$\sigma = \sum_{j \in J_g} x_j; \quad \sigma_s = \sum_{j \in J_s} x_j \quad (7)$$

$$\Delta G_{gr} = G_{gr} - G_w^0 = \frac{2\alpha V_c}{r} - \frac{q^2 V_c}{32\pi^2 r^4} \quad (8)$$

Here  $G_j^0$  is standard molar Gibbs' energy of component  $j$ ;  $G_c$ ,  $G_g$  and  $G_w$  is Gibbs' energy of condensed substances, gaseous substances and liquid water, respectively;  $\Delta G_{gr}$  is correction for dispersity over a droplet of radius  $r$ ;  $J_g$  and  $J_c$  are sets of components of the gas and condensed phases,  $J_s$  is a set of components of solution;  $V_c$  is the molar volume of the condensed phase;  $\alpha$  is surface tension force,  $\epsilon$  is dielectric permittivity of liquid water;  $q$  is the charge of a droplet.

#### MODELING OF AEROSOL WATERING PROCESSES

The effect of surface tension forces on the concentration of salts in the nucleating droplets and on the total amount of liquid phase in the system is investigated with the help of MEIS for the droplets of variable radius. For calculating chemical composition of droplets, assumptions were made that are accepted in microphysics of clouds [3]: 1) heterogeneous system incorporating gas and liquid phases is equilibrium; 2) the liquid phase is a diluted solution of electrolytes containing sulfates, chlorides, hydrocarbonates, nitrates, and cations:

$H^+$ ,  $K^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $NH_4^+$ . Propriety of these assumptions in thermodynamic modeling has been confirmed by previously obtained results of the investigation of composition and size of nucleating droplets, which are consistent with experimental data and calculations of other researchers [9].

In the series of numerical experiments, we calculated the equilibrium radius of droplets formed on the CN of different composition. Energetically most favorable and correspondingly the most probable radius is the one providing the lowest Gibbs' energy of the system ( $G_{sys}$ ). The initial composition of the gas phase (air) in this series of experiments included macro components:  $O_2$ ,  $N_2$ ,  $CO_2$ , and  $H_2O$  (the amount of water in the system corresponded to relative humidity  $f = 99\%$  at pressure  $P = 1012$  hPa). The composition of CN was described by a mixture of condensed substances:  $NaCl$  and  $CaCO_3$ . The solubility of CN was varied by changing the ratio of these two substances:

$$E_m = x_{NaCl} / (x_{NaCl} + x_{CaCO_3}) \quad (9)$$

Here  $x$  is molality, mol/kg. We considered electrically neutral case when the charge  $q = 0$  in eq. (6).

Results of calculations are shown in Figs. 1 and 2, and in Table 1. The dependent variable in the plots is the difference  $\Delta G_{sys}$  between total energy of the disperse system and the energy of the system in which droplet radius is  $r = \infty$  (bulk water).

The following conclusions can be drawn from the analysis of experimental results:

1. The model allows describing the formation of thermodynamically stable liquid-phase aerosol in a multicomponent system, as well as the conditions of stability of the disperse phase.

2. Calculations according to the model predict an inverse dependence of the equilibrium radius of a droplet on the solubility of aerosol particles  $E_m$  (see Table 1); its appearance can be obtained by means of thermodynamic calculations for a given chemical composition of the CN.

3. Since the change in aerosol droplet size distribution with time (aerosol ageing) obeys the

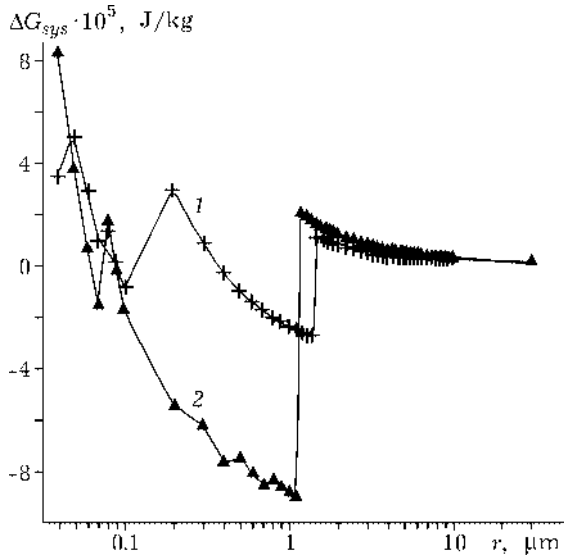


Fig. 1. Dependence of free energy of the system on droplet radius for different  $E_m$  values. The fraction of soluble substance, %: 32 (1), 50 (2).

requirement for the decrease in free energy of the system, the obtained dependencies  $\Delta G_{sys}(r)$  allow determining the direction of the change in distribution at the known CN composition.

4. Even insignificant variations of pressure affect the equilibrium radius substantially (see Fig. 2).

5. It is evident that the equilibrium droplet radius depends to the largest extent on relative humidity, especially if water vapour pressure over a droplet  $P_w(r, \mathbf{x})$  turns out to be close or equal to the saturation pressure. In this case, insignificant change of  $r$  and the corresponding change of  $\mathbf{x}(r)$  lead to a sharp change of  $G_{sys}$ , which is linked with the sub-

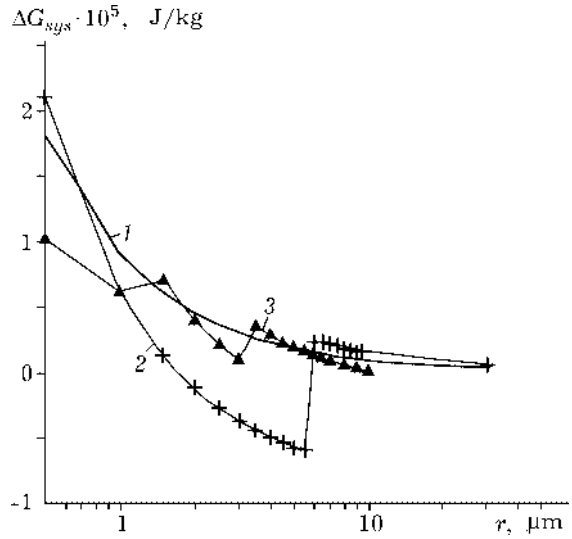


Fig. 2. Effect of pressure on the position of equilibrium radii. Pressure, atm: 0.99 (1), 1.012 (2), 1.02 (3).

stantial increase in the amount of solution in the system.

It should be explained that jumpwise changes of  $G_{sys}(r)$  with variations of  $r$  are linked with the competitive interaction between two factors: 1) curvature of the droplet surface, which increases saturation pressure of water vapour; 2) concentration of dissolved substances, which decrease saturation pressure of the vapour over the solution, in comparison with pure water. Since the decrease in radii is accompanied by the increase in concentration (see Table 1), the mentioned factors change with slope opposition to each other. The diversity of forms of  $G_{sys}(r)$  dependence is induced by the diversity of salt effects in the multicomponent solution. The calculations show that the energy of interaction determining

TABLE 1

Effect of solubility of condensation nuclei on the characteristics of droplets

Characteristic	Value		
$E_m$ , %	32	55	99
$r$ , $\mu\text{m}$	7	6.5	6.12
Equilibrium concentration, kg/kg:			
$\text{H}_2\text{O}(\text{liq})$	$1.59 \cdot 10^6$	$3.12 \cdot 10^6$	$3.83 \cdot 10^6$
$\text{Ca}^{2+} \cdot 2\text{HCO}_3^-$	$4.50 \cdot 10^8$	$4.75 \cdot 10^8$	$1.10 \cdot 10^8$
$\text{Na}^+ \cdot \text{HCO}_3^-$	$2.47 \cdot 10^8$	$1.79 \cdot 10^8$	$4.69 \cdot 10^8$
$\text{Ca}^{2+} \cdot 2\text{Cl}^-$	$1.63 \cdot 10^8$	$3.14 \cdot 10^8$	$3.10 \cdot 10^8$
$\text{Na}^+ \cdot \text{Cl}^-$	$5.50 \cdot 10^8$	$8.03 \cdot 10^8$	$1.64 \cdot 10^7$

the shape of the equilibrium size distribution of aerosol droplets turns out to be 8–10 orders smaller than the energy of chemical interactions. In particular, for this reason, the equilibrium droplet size distribution is strongly dependent on the nature and composition of the CN.

## CONCLUSION

We intend to apply the described procedure to the obtaining of theoretical dependencies  $r(E_m)$  for  $T$ ,  $P$ , and  $f$  variables taking into account the published data on the composition of CN of both natural and anthropogenic origin. In particular, this will allow us to specify the data on the effect of meteorological parameters on microphysical characteristics of haze, clouds and fog. In addition, a strict description of heterophase transformations in the atmosphere is of interest for the investigation of the behaviour of anthropogenic admixtures. The problem of estimating the effect of these processes on optical characteristics that determine the role of aerosol as a climatic factor is also urgent.

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