Thermodynamic modeling of the atmospheric liquid-phase aerosol

E.V. Kuchmenko, A.V. Keiko, and E.V. Molozhnikova

Institute of Power Systems,
Siberian Branch of the Russian Academy of Sciences, Irkutsk

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A thermodynamic model of extreme intermediate states is used to describe generation of liquid-phase aerosol in the polluted atmosphere. Fog droplets in the model are presented as a diluted solution of strong electrolytes, which is described using the Debye–Hueckel statistical theory. At the first stage, the amount and composition of the liquid phase were calculated (neglecting surface tension) at varying amount of harmful admixtures, temperature, and pressure. Then the equilibrium ion concentrations and the absorbability of droplets of different radius were studied. The influence of the initial concentrations of SO_2 and NO_x on the total amount of the solution simulating liquid-phase aerosol under the atmospheric conditions is estimated.

As known, the anthropogenic impact leads to the change in the composition, amount, and size of condensation nuclei (CN), thus affecting the repetition and microphysical characteristics of hazes, fogs, and precipitation in cities. Moistening of CN due to deliquescence starts in the atmosphere already at the relative humidity about 30%, and formation of haze starts at 80% (Ref. 1).

Complex processes in the atmosphere, including phase transitions and chemical interactions, for which the mechanisms of reactions are not still studied in detail, are described with the help of thermodynamic models. The undoubted advantage of this approach is almost complete absence of restrictions on the list of substances included into consideration. Unlike the methods of chemical kinetics, which are traditionally used for modeling transformations of substances in the polluted atmosphere, thermodynamic model does not need information on the specific mechanism of reactions, their rates, and intermediate products.

Kaganovich and Filippov in Ref. 2 described the thermodynamic model of extreme intermediate states (MEIS), which allows one to study not only the final equilibrium state of a system, but also a number of intermediate (incomplete) equilibrium states, which the system takes at relaxation to the final equilibrium state:

find the maximum of

$$\mathbf{F}(\mathbf{x}, \mathbf{y}) = \sum_{j \in J^{\text{ext}}} c_j x_j \Big/ \sum_{j \in J^0} g_j y_j \tag{1}$$

under conditions

$$\sum_{j=1}^{l} m_j y_j = 1, \tag{2}$$

$$\mathbf{A}\mathbf{x} = \mathbf{b}(\mathbf{y}), \tag{3}$$

$$\mathbf{A}\mathbf{y} = \mathbf{b}(\mathbf{y}), \tag{4}$$

$$\alpha_k \sum_{j \in J_k} y_j \le \mathbf{y}_k \le \beta_k \sum_{j \in J_k} y_j, \quad k \in K, \tag{5}$$

$$D_t(y) = \{x : G(x^{\text{eq}}) \le G(x) \le G(y);\ G(x') \ge G(x'')\}, \tag{6}$$

$$G(\mathbf{x}) = \sum_{j \in J} G_j x_j, \tag{7}$$

$$G_j = f_j(\mathbf{x}), \tag{8}$$

$$x_j \ge 0, \quad y_j \ge 0, \tag{9}$$

where $\mathbf{x} = (x_1, \ldots, x_n)^{\mathrm{T}}$ is the vector of molar amounts of the mixture reagents; $\mathbf{y} = (y_1, \ldots, y_l)^{\mathrm{T}}$ is the vector of molar amounts of the initial reagents, $\mathbf{y} \subset \mathbf{x}$; J^{ext} is the set of the components, whose extreme concentration is to be determined; c_j is the coefficient ranking the insalubrity (or other property) of the jth component of the vector x, $c \ge 0$; J^0 is the set of the initial components that affect atmospheric pollution; g_j is the coefficient ranking the effect of the jth component on atmospheric processes, $g_j \ge 0$; $\mathbf{m}$ is the molar mass; $\mathbf{A}$ is the $m \times n$ matrix of element contents in the system components; α and β are coefficients; k is the inequality (equality) index; K is the set of the initial reagents, whose amounts can be restricted; J_k is the set of the initial reagents, which are accounted for in the kth restriction; $D_t(y)$ is the set (domain) of thermodynamic accessibility from the initial state; G and G_j is the Gibbs free energy, respectively, of the system and the mole of its jth component; $\mathbf{x}^{\text{eq}}$ is the point of the global (final) equilibrium of the system; $\mathbf{x}'$ and $\mathbf{x}''$ are the points on thermodynamically allowed trajectories in the spaces of composition, and $\mathbf{x}'$ precedes $\mathbf{x}''$; J is the set of components taken into account. The molar free energy $\mathbf{G}(\mathbf{x})$ was calculated differently for the following phases: gas, free condensed substances, ideal solution, actual solution, surface gas, and the finely dispersed phase.[2]

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As known, the water droplets in the atmosphere never consist of only pure water, because moistening of solid CN particles needs far lower energy, than the formation of pure liquid water nuclei. Therefore, at the next stage of thermodynamic description of these processes, diluted solutions of electrolytes were included in the initial composition. The implemented version of MEIS allows one to model solutions of strong electrolytes using the Debye–Hueckel statistical theory. The Gibbs energy of one mole of the jth component of the solution can be presented as

$$G_j = G_j^0 + RT \ln \frac{x_j}{\sigma_s} + RT \ln\gamma_j, \qquad (10)$$

where σ_s is the total number of moles of the solvent and the dissolved substances; γ_j is the rational (related to the molar fraction) coefficient of activity of the jth component; G_j^0 is the standard Gibbs energy of the jth component; R is the universal gas constant; T is the temperature. The values of γ_j are determined from the following equations:

$$\log\gamma_{\pm j} = -\frac{\varphi\, |Z_{1j}\, Z_{2j}|\, I(x_e)^{0.5}}{1 + I(x_e)^{0.5}} + \Psi(x_e), \qquad (11)$$

$$\varphi = 1.825 \cdot 10^6/(\varepsilon^{1.5}\, T^{1.5}), \qquad (12)$$

$$I \approx \frac{27.778}{x_{H_2O}} \sum_{j \in J_\pm} (Z_{1j}^2\, \nu_{1j} + Z_{2j}^2\, \nu_{2j}), \qquad (13)$$

where $\Psi = 0.1\, |Z_{1j}\, Z_{2j}|$; $\gamma_{\pm j}^{\nu_j} = \gamma_{+j}^{\nu_j}\, \gamma_{-j}^{\nu_j}$, $\nu_j = \nu_{1j} + \nu_{2j}$, ν_{1j} and ν_{2j} are stoichiometric coefficients of the cation and anion in the reaction of dissociation of the jth electrolyte; φ and Ψ are coefficients; Z_{1j} and Z_{2j} are the charges of, respectively, the cation and anion, into which the jth electrolyte dissociates; I is the ion force of the solution: x_e is the vector of the molar amounts of electrolytes; ε is the water dielectric constant; $J_\pm$ is the set of ion pairs in the solution.

Using this approach, we estimated the effect of changes in the composition of gas phase on the ion composition of condensed droplets and pressure of saturated water vapor over droplets of different composition (Table 1).

To estimate quantitatively the effect of atmospheric pollution on condensation processes using the equilibrium model of solutions, we accept the following assumptions that are commonly accepted in cloud microphysics:

– a heterogeneous system including gas and liquid phases is in equilibrium;

– the liquid phase is an unsaturated solution of electrolytes, including sulfates, nitrates, chlorides, and hydrocarbonates.

Besides, at the first stage we assume that the liquid phase has a plane infinite surface (the system is heterogeneous, but spatially homogenous).

Table 1. Example of calculation of the liquid phase in the atmosphere (T = 298 K, P = 1 atm)

Substance	G_j, J/mol	y, mol/kg	x^{eq}, mol/kg
	Gas phase		
HNO_3	−213410	$5.11 \cdot 10^{-8}$	$7.22 \cdot 10^{-12}$
O_3	70613.5	$1.42 \cdot 10^{-6}$	0.0
O_2	−61110	7.18	7.16
NO_2	−37345.4	$4.58 \cdot 10^{-7}$	$1.44 \cdot 10^{-11}$
NO	28486.8	$6.06 \cdot 10^{-12}$	$4.62 \cdot 10^{-10}$
N_2O_5	−92682	$2.91 \cdot 10^{-10}$	0.0
CO	−169407	$7.11 \cdot 10^{-6}$	0.0
H_2	−38904.9	$1.96 \cdot 10^{-5}$	0.0
N_2	−57071.6	26.7	26.7
H_2O	−298051	1.03	1.04
CH_4	−130107	$6.13 \cdot 10^{-3}$	$1.28 \cdot 10^{-17}$
CO_2	−457182	$1.19 \cdot 10^{-2}$	$1.80 \cdot 10^{-2}$
C_2H_4	−12921.6	$1.74 \cdot 10^{-9}$	0.0
C_3H_6	−59130.2	$1.87 \cdot 10^{-9}$	0.0
SO_2	−370743	$6.55 \cdot 10^{-7}$	$4.64 \cdot 10^{-12}$
CH_3Cl	−151824	$3.50 \cdot 10^{-7}$	0.0
HCl	−147978	0.0	$2.05 \cdot 10^{-8}$
	Solution		
L:H_2O	−306714	$3.50 \cdot 10^{-5}$	$5.16 \cdot 10^{-4}$
$H^+\ NO_3^-$	−243873	$3.50 \cdot 10^{-14}$	$1.25 \cdot 10^{-7}$
$H^+\ HCO_3^-$	−713359	$3.50 \cdot 10^{-14}$	$1.28 \cdot 10^{-7}$
$2H^+\ SO_4^{2-}$	−1800384	$3.50 \cdot 10^{-14}$	$6.55 \cdot 10^{-7}$
$H^+\ Cl^-$	−177537	$3.50 \cdot 10^{-14}$	$3.30 \cdot 10^{-7}$

At the 100% relative humidity of air, droplets of fog (cloud) are already much diluted solutions.[3] Thus, in our example at the initial SO_2 content at the level of the maximum permissible concentration (MPC), 0.001 molal solution of H_2SO_4 was obtained in equilibrium. This means that the solution has practically no effect on the saturation pressure. However, moistening of CN in the atmosphere occurs, as known, at the relative humidity of about 80% and even lower. Condensation droplets and fog droplets produced at the humidity lower than 100% form a solution, whose concentration is 10–20% and higher. Thus, the use of the thermodynamic model allows one to study the effect of the composition of a condensation droplet on the processes in some its vicinity.

We have performed a series of calculations, in which the content of SO_2 varied roughly from 0.2 to 20 MPC (from $1.19 \cdot 10^{-7}$ to $1.19 \cdot 10^{-5}$ mol/kg) at the constant parameters $T = 298$ K, $P = 1.0$ atm, and humidity about 30%. We studied the resulting final equilibrium state. The equilibrium concentration of H_2SO_4 in the solution remained almost unchanged nearby 8%, but the total amount of the solution in the system increased almost two orders of magnitude. Consequently, pollution of the atmosphere with sulfur oxides favors the increased generation of the liquid phase in the form of haze, rain, and fog droplets and the decrease of SO_2 in the gas phase. This conclusion agrees with observations and serves a qualitative justification of the correctness of the model borrowed from Ref. 4.

The equilibrium composition of the solution imitating haze or fog droplets mostly corresponds to the measurement data and calculations by other authors (Table 2) (Ref. 3).

Table 2. Comparison of the calculated (equilibrium) composition of the solution with observations of precipitation composition

	NO_3^-	HCO_3^-	SO_4^{2-}	Cl^-	NO_3^-	HCO_3^-	SO_4^{2-}	Cl^-
	mg/l				%			
1	2.65	0.4	6.5	1.3	24.4	4.0	60.1	11.6
2	1.7	1.5	7.4	2.4	13.1	11.5	56.9	18.5
3	0.5	3.0	3.0	2.0	5.9	35.3	35.3	23.5
4	1.8	7.7	10.5	2.5	8	34.2	46.7	11.1
5	1.8	2.4	4.1	1.3	19.1	25.1	42.8	13.1

Notes: 1 – calculated results, 2 – Baltic areas, Leningrad Region, 3 – Krasnoyarsk Region, 4 – industrial regions of the USA, 5 – averaged data of Ref. 3.

The following calculated results showed that the concentration of a solution in the equilibrium state is affected by the amount of gaseous pollutants in the initial system, as well as by the amount of liquid water, which is determined by the relative air humidity (Fig. 1). Here curves *1* and *2* are the results of thermodynamic modeling at different initial compositions (0.5 MPC NO_2 and 5 MPC NO_2 in the gas phase), curves *1**, *2**, *3**, and *4** were obtained using the empirical equation

$$X^{-1} = 0.01(1 - \Phi M_\mathrm{w}/M \ln f), \tag{14}$$

where X is the concentration of the solution, in %; Φ is the empirically determined practical osmotic coefficient of a complex ion solution; M and M_w are the molar masses of the solution components (mean) and water; f is the relative air humidity. Curves *1*–4** differ by the values of M, i.e., by the ratios of the solution components.

The next step in modeling of liquid-phase processes in polluted atmosphere is the description of surface tension forces, i.e., transition from consideration of processes above a plane surface of pure water to analysis of generation of droplets with the finite radius r. As known, the saturation pressure above the droplet increases as compared to the pressure above the plane surface of a liquid, and the change of the chemical potential depending on the droplet radius is determined by the surface tension force of a given substance (σ):

$$\Delta G = 2\sigma v/r, \tag{15}$$

where v is the modal volume of water; r is the droplet radius.

A series of control calculations for pure water allows us to speak about good agreement (± 0.015 g/kg) of the results with the known Kelvin equation:

$$P_r = P_\infty \exp(2\sigma v/rRT). \tag{16}$$

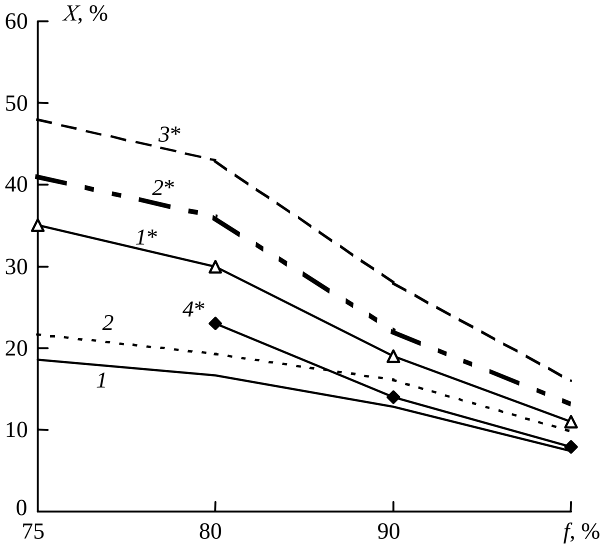

Fig. 1. Change of the solution concentration at the increasing relative humidity (T = 25°C): calculated results (*1* and *2*) and literature data[3] (*1*–4**).

The dependence of the solution concentration on the droplet radius is shown in Fig. 2. Obviously, the effect of the nuclei composition prevails at $r > 0.5$ μm, and the effect of the radius begins to prevail for fine particles. It should be explained that the curves *1**, *2**, and *3** have been calculated by the equation

$$X^{-1} = 9.1 \cdot 10^4 \frac{\Phi M_\mathrm{w}}{M} r \tag{17}$$

at variation of the solution composition, whereas curves *1′* and *2′* have been calculated based on thermodynamics for different initial compositions (0.5 MPC NO_2 and 5 MPC NO_2 in the gas phase).

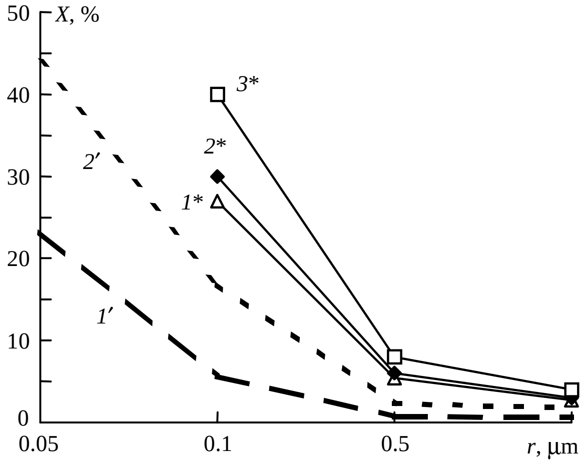

Fig. 2. Concentration of the solution (X) in droplets of different radius: literature data[3] (curves *1**, *2**, and *3**) and calculated results (curves *1′* and *2′*).

It should be emphasized once more that thermodynamic modeling, in contrast to other methods, allows the composition of gaseous pollutants and components of the electrolyte solution to be changed within a wide range. Thus, it becomes possible to study the effect of the initial concentration of gaseous pollutants on the composition of the solution, as well as on the absorbability of droplets of different radius. Consequently, thermodynamic modeling allows imitating the mechanisms of redistribution of the pollutants between phases and estimating the effect of such meteorological conditions as air humidity and presence of haze and fog droplets on the composition and concentration of secondary pollutants.

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