

Thermodynamic simulation of anthropogenic influence on chemical composition of precipitation

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A new approach to studying the condensation processes in the polluted atmosphere, based on the thermodynamic models, is presented. The thermodynamic models of extreme intermediate states (MEIS) can be used for analysis of system states in the course of the system relaxation toward final equilibrium. Raindrops are modeled as a diluted solution of strong electrolytes, using Debye-Hueckel statistical theory. The methods of description of surface effects, used in the model, are discussed. The mathematical simulation results are compared with the statistically analyzed data of observations of chemical composition of precipitation in different Eastern Siberian regions. Theoretical and experimental estimates of the dependence of droplet ion composition in the atmosphere on the concentration of gaseous pollutants and composition of the condensation nuclei are presented.

The atmosphere is an open heterogeneous system exchanging substance and energy with a non-equilibrium environment.

It is normally believed that the atmospheric chemistry admits no thermodynamic approach in principle. Actually, as at low temperatures most of the chemical reactions are very slow, the traditional

methods of seeking finite equilibrium states cannot describe the atmospheric processes adequately.

Main atmospheric pollutants have nearly zero concentration in the final equilibrium state. From Table 1 it is seen that the observed hazardous concentrations of these species in air correspond to intermediate partial equilibrium states.

Table 1. Equilibrium and extreme concentrations of some pollutants in the atmosphere ($T = 298$, $P = 1000$ hPa)

Species		Gibbs free energy J/mol	State, mol/kg		
Name	Formula		Initial	Equilibrium	Extreme
Nitrogen	N ₂	-57072	26.79	26.79	-
Oxygen	O ₂	-61110	7.19	7.18	-
Water vapor	H ₂ O	-298051	1.04	1.05	1.05
Carbon dioxide	CO ₂	-457182	1.20·10 ⁻²	1.79·10 ⁻²	1.79·10 ⁻²
Methane	CH ₄	-130107	5.83·10 ⁻³	0.00	-
Carbon monoxide	CO	-169407	7.00·10 ⁻⁶	0.00	-
Hydrogen	H ₂	-38905	1.92·10 ⁻⁵	0.00	-
Ozone	O ₃	70613	1.39·10 ⁻⁶	0.00	-
Sulfur oxide	SO ₂	-370743	6.42·10 ⁻⁷	0.00	7.00·10 ⁻⁷
Sulfuric acid	H ₂ SO ₄	-821886	0.00	7.00·10 ⁻⁷	7.00·10 ⁻⁷
Nitric acid	HNO ₃	-213410	5.01·10 ⁻⁸	5.73·10 ⁻⁸	1.38·10 ⁻¹
Nitrogen oxides	NO	28487	5.90·10 ⁻¹²	6.17·10 ⁻¹⁵	6.55·10 ⁻²
	NO ₂	-37345	4.19·10 ⁻⁹	4.27·10 ⁻⁹	1.18·10 ⁻¹
Chlorine	Cl ₂	-66450	0.00	6.44·10 ⁻⁷	-
Hydrogen chloride	HCl	-147978	1.17·10 ⁻⁸	3.02·10 ⁻⁷	1.59·10 ⁻⁶
Trichloroethane	C ₂ H ₃ Cl ₃	-240257	3.43·10 ⁻⁷	0.00	5.30·10 ⁻⁷
Peroxyacetyl nitrate (PAN)	CH ₃ COONO ₃	-220359	0.00	0.00	3.98·10 ⁻³
Hydrocarbons	C ₂ H ₄	-12922	1.70·10 ⁻⁹	0.00	-
	C ₃ H ₆	-59130	1.84·10 ⁻⁹	0.00	-
Benzapilene	C ₂₀ H ₁₂	245377	0.00	0.00	4.65·10 ⁻⁴

Thermodynamic atmospheric models

Mathematically, the problem of determining intermediate equilibrium states satisfying certain conditions is formulated as a modification of the general model of extreme intermediate states (MEIS).^{1,2}

The research area of our concern here had included until presently only few interrelated atmospheric thermodynamics problems such as (1) estimation of the effect of primary pollutants on concentration of the secondary admixtures and (2) the processes of condensation and precipitation formation, and others.¹

The problem of determining an equilibrium concentration of water vapor has great practical importance because, without its solution, it is impossible to determine the conditions for formation of fog and smog in the atmosphere, as well as the conditions for formation of acid rains.^{3,4} Many harmful substances do form in aqueous solutions – on aerosol surface and in rain, haze, and fog droplets.^{5,6} The thermodynamic laboratory at MIPS SB RAS is presently developing the following models with gradually increasing level of complexity: (1) condensation of water vapor over a planar liquid surface; (2) formation of spheroidal droplets with the account of surface tension (α); (3) formation of droplets possessing an electric charge and experiencing surface tension; and (4) dissolving of harmful substances in electrically charged particles subject to α effect.

The first simplest model is a traditional final-equilibrium block of the model of extreme intermediate states (MEIS).¹

Let us determine

$$\min \left[G = \sum_{j \in J_g} \left(G_j^0 + RT \ln \frac{x_j}{\delta} \right) x_j + \sum_{j \in J_c} G_j^0 x_j \right] \quad (1)$$

provided that

$$\mathbf{Ax} = \mathbf{b}, \quad (2)$$

$$x_j \geq 0, \quad (3)$$

where G and G_j^0 are the Gibbs energy of the system and standard Gibbs energy of the mole of the j th component, respectively; J_g and J_c are the sets of indices of gas- and condensed-phase components; T is temperature; R is the universal gas constant; \mathbf{x} is the vector of the number of moles of the components in reacting mixture; δ is the total amount of moles of gas-phase components; \mathbf{A} is the $m \times n$ matrix of abundance of species in the components of the system; m is the number of material balances; \mathbf{b} is the vector of amounts of the moles of elements.

To increase model complexity, it is necessary to describe the components of Gibbs energy, determined by surface tension and electrical charges of particles. Correspondingly, it is necessary, first, to consider the conditions of equilibrium between droplet and surrounding vapor:

$$\min \left[\Delta G_{dr} = \alpha 4\pi r^2 - \left(\frac{4}{3} \pi r^3 / V_c \right) (G_g - G_c) \right], \quad (4)$$

where ΔG_{dr} is the change of the Gibbs energy of condensed water during droplet growth; r is the droplet radius; V_c is the molar volume of the condensed-phase component; $G_g - G_c$ are the molal Gibbs energies of gas- and condensed-phase components, respectively.

Secondly, one more component of molal Gibbs energy, namely G_{el} , should be introduced to estimate the influence of the electrical charge of particles.

With the account of action of charge (q),⁷ the conditions of equilibrium of the drop with the surrounding vapor become

$$G_{gr} - G_c = \frac{2\alpha V_c}{r} - \frac{q^2 V_c}{32\pi^2 r^4}. \quad (5)$$

Then, the model of condensation of water vapor in the atmosphere on electrically charged particles has the following form.

Determine now

$$\min \left[\sum_{j \in J_g} \left(G_j^0 + RT \ln \frac{x_j}{\sigma} \right) x_j + \left[G_{\text{H}_2\text{O}(c)}^0 + \frac{3\alpha V_c}{r(G_{gr})} + \frac{3q^2 V_c}{32\pi^2 r^3} \left(\frac{1}{r} + \frac{1}{a\epsilon} \right) \right] x_{\text{H}_2\text{O}(c)} + \sum_{j \in J_c} G_j^0 x_j \right] \quad (6)$$

provided that

$$\mathbf{Ax} = \mathbf{b}; \quad (7)$$

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

$$G_{gr} = G_{\text{H}_2\text{O}(g)}^0 + RT \ln \frac{x_{\text{H}_2\text{O}(g)}}{\sigma}, \quad (9)$$

$$x_j \geq 0, \quad 0 \leq r \leq \left(\frac{3}{4\pi} \frac{x_{\text{H}_2\text{O}(c)} M_{\text{H}_2\text{O}}}{\rho_{\text{H}_2\text{O}(c)}} \right)^{1/3}, \quad (10)$$

where $M_{\text{H}_2\text{O}}$ and $\rho_{\text{H}_2\text{O}(c)}$ are molar mass and density of condensed water; ϵ is the dielectric constant; a is the ion radius.

Analysis of the results obtained by numerical simulation

Interpretation of the results obtained using a thermodynamic simulation requires a thorough knowledge of both the method used and specific features of the process studied. As has already been pointed out in literature,² the approach considered here well reproduces, on the whole, the concentration of dissolved germ droplets as a function of their radius and relative air humidity that determines the amount of liquid water in the system.

Next, we analyzed the influence of chemical composition of the condensation nuclei on the composition of precipitation and compared the obtained results with data of observations in the southern Eastern Siberia.

To facilitate the experiment-to-theory comparison, we performed a preliminary statistical processing of the results of chemical analysis obtained in hydrochemistry laboratory at Limnological Institute, SB RAS. Only data for 1999 (at three sites in Irkutsk, Mondy, and Listvyanka) were considered. Figure 1 presents annually mean observation data (composition of precipitation and cations) and mean multiyear characteristics averaged over natural climatic zones.⁶ Evidently, our region has much less sodium cations, but markedly more Ca and NH_4 , than zonal mean data suggest. Analogous analysis for anions has shown that, compared with literature data, Irkutsk and Listvyanka have much higher SO_4^{2-} content. An appreciable increase in the ammonium sulfate content is likely explained by the anthropogenic sources of aerosols in the region.

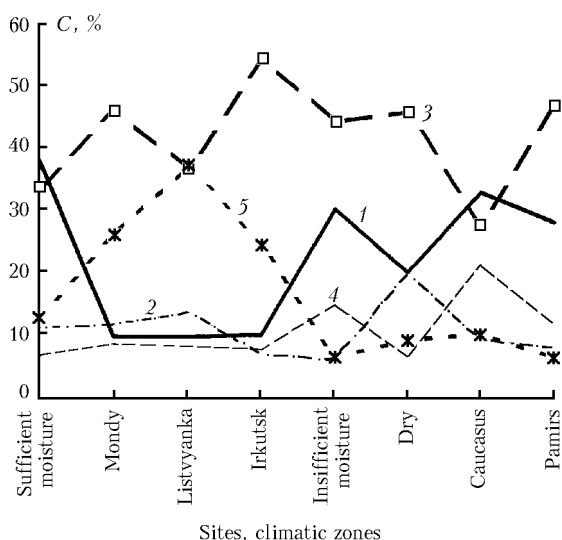


Fig. 1. Composition of precipitation in different natural climatic zones of the former USSR: Na (1); K (2); Ca (3); Mg (4); NH_4 (5).

Seemingly, the anthropogenic factors can also be considered responsible for the fact that the concentration of sulfate and hydrogen carbonate ions, as well as of Ca, Na, and some other ions, in precipitation in Irkutsk is almost three times higher in winter than in summer months. Likewise, in Mondy, in winter period the concentrations of all anions and calcium also substantially increase, though, possibly due to wintertime increase of wind velocity and transport of soil aerosols from neighboring Mongolia.

For days with precipitation in 1999, we performed calculations by the back trajectories technique using trajectory model and information available from Internet at <http://www.arl.noaa.gov>. All in all, 7 different trajectory types were identified for air masses at heights 3000 and 5000 m. No significant correlation between the trajectory type and composition of

precipitation was revealed. However, after the composition was averaged over trajectory types, we obtained very characteristic pattern: in Irkutsk, the concentration of Ca^{2+} , SO_4^{2-} , and HCO_3^- ions is maximum for the north-westerly trajectory types, i.e., when precipitation forms over industrial regions of Irkutsk Region and Krasnoyarsk Krai. When precipitation originates from south and southwest, the amount of ions is lowest in it. At the site in Mondy, the greatest amount of main ions was found in precipitation originating from south-west, namely, Mongolia and Kazakhstan, since the dust load of air masses and natural mineralization of the precipitation is known to increase from north to south.

In the thermodynamic simulation of condensation processes, the aerosols in the system were modeled as solid salts of metals, as well as ammonium salts. We considered a heterogeneous but spatially homogeneous system, so aerosol particle and droplet sizes were not taken into account (Table 2).

Table 2. Exemplary simulation of composition of precipitation in the atmosphere ($T = 298 \text{ K}$, $P = 1 \text{ atm}$)

Species	Gibbs free energy G_0 , J/mol	State, mol/kg	
		Initial Y	Equilibrium X^{eq}
<i>Gas phase</i>			
N_2	-57071.6	26.7	26.7
O_2	-61110	7.15	7.15
CO_2	-457182	$1.19 \cdot 10^{-2}$	$1.19 \cdot 10^{-2}$
H_2O	-298051	1.22	1.06
O_3	70613.5	$1.42 \cdot 10^{-6}$	0.0
NO_2	-37345.4	$4.26 \cdot 10^{-7}$	$3.40 \cdot 10^{-11}$
NO	28486.8	$6.04 \cdot 10^{-12}$	0.0
HNO_3	-213410	$5.09 \cdot 10^{-8}$	$1.81 \cdot 10^{-11}$
CH_3Cl	-151824	$3.50 \cdot 10^{-7}$	0.0
SO_2	-370743	$3.49 \cdot 10^{-7}$	$2.48 \cdot 10^{-11}$
<i>Aerosol</i>			
C:CaSO ₄	-1466387	$3.49 \cdot 10^{-7}$	$2.48 \cdot 10^{-11}$
C:Na ₂ CO ₃	-1169418	$3.49 \cdot 10^{-7}$	$2.48 \cdot 10^{-11}$
<i>Solution of droplets</i>			
$\text{H}_2\text{O}_{(\text{c})}$	-306714	$3.49 \cdot 10^{-4}$	0.165
H^+NO_3^-	-243873	$3.49 \cdot 10^{-14}$	$1.96 \cdot 10^{-7}$
$\text{Ca}^{2+}2\text{NO}_3^-$	-1027536	$3.49 \cdot 10^{-14}$	$6.35 \cdot 10^{-8}$
Na^+NO_3^-	-508125	$3.49 \cdot 10^{-14}$	$1.54 \cdot 10^{-7}$
H^+HCO_3^-	-713359	$3.49 \cdot 10^{-14}$	$8.47 \cdot 10^{-7}$
$\text{Ca}^{2+}2\text{HCO}_3^-$	-1966506	$3.49 \cdot 10^{-14}$	$8.94 \cdot 10^{-9}$
$\text{Na}^+\text{HCO}_3^-$	-977610	$3.49 \cdot 10^{-14}$	$3.53 \cdot 10^{-8}$
$\text{H}_2^+\text{SO}_4^-$	-900192	$3.49 \cdot 10^{-14}$	$2.68 \cdot 10^{-7}$
$\text{Ca}^{2+}\text{SO}_4^-$	-1439981	$3.49 \cdot 10^{-14}$	$2.33 \cdot 10^{-7}$
$\text{Na}^{2+}\text{SO}_4^-$	-1428694	$3.49 \cdot 10^{-14}$	$1.96 \cdot 10^{-7}$
H^+Cl^-	-177537	$3.49 \cdot 10^{-14}$	$1.46 \cdot 10^{-7}$
$\text{Ca}^{2+}\text{Cl}_2^-$	-894863	$3.49 \cdot 10^{-14}$	$4.32 \cdot 10^{-8}$
Na^+Cl^-	-441788	$3.49 \cdot 10^{-14}$	$1.16 \cdot 10^{-7}$
M, kg	-	0.0286	0.0286
G, J	-	-68335.8	-68336.6

As expected, addition of cations of metals had little effect on thermodynamic properties of solution of droplets. The concentration of ions in the solution was found to be almost proportional to those in solid phase. However, the concentration of solution and amount of liquid water is affected somewhat by solubility of the compounds. The competition between cations is small and does not depend on temperature.

The method of thermodynamic simulation can be used to study the influence of temperature on the composition of droplets (Fig. 2). Evidently, the dependence of concentrations on temperature is most complicated for hydrogen carbonates. As known, the hydrogen carbonates equilibrium between calcium bicarbonate, contained in the solution, dissolved carbon dioxide, and atmospheric carbon dioxide is controlled to a large extent by temperature.⁷ Moreover, the equilibrium state of the atmosphere is typically characterized by a higher relative amount of hydrogen carbonates in solution of droplets at larger air humidity and liquid water content of the precipitation.

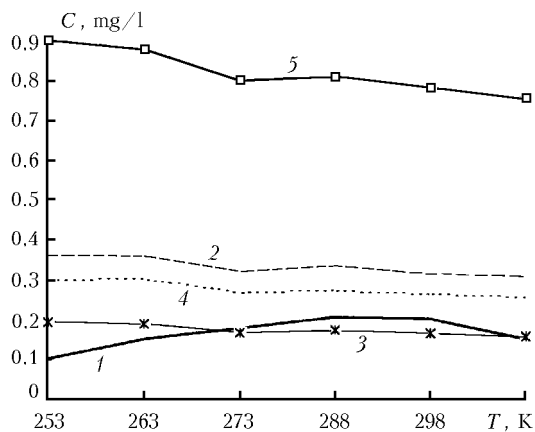


Fig. 2. Influence of temperature on equilibrium composition of solution: $\text{H}(\text{HCO}_3)$ (1); $(\text{NH}_4)_2\text{SO}_4$ (2); NH_4Cl (3); CaCl (4); CaSO_4 (5).

It should be noted that the data given in Table 2, as an example, characterize a polluted atmosphere, because it has over 0.6 maximum permissible concentration (MPC) of sulfur oxide, and almost 2 MPC of aerosol (inorganic dust). At the same time, the composition of anions in the model is very close to what is observed in Irkutsk in winter (Table 3).

In contrast to other methods, in thermodynamic simulation it is possible to vary the composition of gas-phase pollutants and solid particles, as well as

components of the electrolytic solution, within wide limits. This allows one to estimate the interrelations between the concentration of different pollutants and composition of rain, haze, or fog droplets. In addition, the study of the influence of radius and composition of germ droplets and condensation nuclei on the intensity of their watering becomes possible.

Table 3. Chemical composition of precipitation (anions) derived from experimental and calculated data (%)

Station, season	HCO_3^-	SO_4^{2-}	NO_3^-	Cl^-
Experiment				
Mondy, summer	24.11	31.66	20.19	24.04
Mondy, winter	42.74	22.55	17.09	17.62
Irkutsk, summer	31.62	43.59	15.67	9.12
Irkutsk, winter	29.38	41.15	20.44	9.02
Calculation				
	29.10	43.96	18.30	8.64

Refined model versions supposedly will make it possible to study the effects on surface of liquid and solid aerosols, as well as to account for gravity and treat more correctly the properties of real solutions.

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