

AIR IONS AND ELECTRICAL AEROSOL ANALYSIS

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Introduction

Researchers have been interested in the chemical composition of small ions since the first quarter of the 20th century [1]. Experimental study of the chemical composition of ions in the troposphere is a complicated task. Measurements of ion electric mobilities give only approximate information about the masses and sizes of ions [2]. Mass-spectrometric studies in the troposphere were carried out only since 1983 [3] and data obtained contained but limited information: only the masses of the cores (more stable parts) of the ions were found out. This explains the interest in theoretical modeling of ion evolution. The modeling has been carried out mostly on the basis of the methods of chemical kinetics: proceeding from the known ion-molecular reactions and the chemical composition of the troposphere, respective differential equations are composed, and the temporal changes of ion concentrations are calculated till the steady state is reached.

The foundation of the modern conception of the evolution of tropospheric small ions was laid down in [4], where the possible transformation processes of ions have been dealt with mainly qualitatively. The importance of ion-molecular reactions has also been pointed out. However, when the paper [4] was published, only a relatively small number of rate constants of ion-molecular reactions were known.

Subsequent research of major importance has been concerning quantitative modeling of ion evolution up to an age of 1 ms [5,6]. $O_2^-(H_2O)_n$ were found to be dominant negative ions and $H_3O^+(H_2O)_k$ dominant positive ions. These results were supported by experimental results. The steady state of negative tropospheric ions has been computed in [7]. In comparison with the paper [5] considerably more ion-molecular reactions and neutral compounds have been taken into account. It has been found out that in the steady state the cluster ions $NO_3^-(H_2O)_k(HNO_3)_m$ are dominant, there are less clusters with the cores HSO_4^- . It should be noted that ions of the same type have also been measured with a mass spectrometer [3].

Ion evolution with a considerably expanded number of reactions and neutral compounds has been modeled in the papers [8,9]. Below we will mainly summarize the results of these papers.

1. Description of the method

1.1. Characterization of the system of equations and previous methods of solution

The formation, evolution, and decay of small tropospheric ions can be mathematically described by the following system of differential equations:

$$\frac{dY}{dt} = AY - BY + Q, \quad (1)$$

where Y is the vector of ion concentrations,

A is the matrix describing the rates of ion-molecular reactions,

B is the matrix describing the decay of ions,

Q is the vector of the rate of ion generation.

The elements a_{jk} of matrix A are products of the rate constants of the respective ion-molecular reactions (where an ion with the number k becomes an ion with the number j) and the concentrations of the neutral compounds participating in the reactions [5,6]. In the modeling of small tropospheric ions the concentrations of neutral compounds are usually considered to be constant, in this case matrix $A = \text{const}$.

By the decay of ions we understand both recombination with the small ions of the opposite sign and attachment to aerosol particles. In both cases the small ion is lost. Thus the elements of matrix B can be expressed by

$$b_{jk} = \delta_{jk}(an + \beta Z), \quad (2)$$

where δ_{jk} is the symbol of Kronecker,

a is the coefficient of recombination,

n is the total concentration of small ions,

β is the effective coefficient of attachment to aerosol particles,

Z is the concentration of aerosol particles [7,10].

Evidently $n = \sum y_j(t)$, (3)

where $y_j(t)$ are the concentrations of particular ion species.

For the modeling of ion evolution the system (1) is to be solved. In principle this could yield both the evolution and the steady state, but the solution is complicated by the following reasons:

- the system (1) is large (the number of equations in the order of magnitude of 100),
- the system (1) is nonlinear even on the assumption of constancy of matrix A ,
- the system (1) is stiff as the elements of matrix A differ from one another up to 10^{11} times.

Due to the solution difficulties, the system (1) has been solved partially. In [5,6] only the linear system

$$\frac{dY}{dt} = AY \quad (4)$$

has been solved using the Runge-Kutta method. The Runge-Kutta method is widely used for the solution of differential equations, but it is not suitable for the solution of stiff equation systems in the case of a long domain of integration. The Gear method has been used for the solution of stiff differential equations in the work [11], but the experience of the authors of that work and of the authors of the present paper shows that difficulties arise also with Gear method.

In the paper [7] only the steady problem

$$\frac{dY}{dt} = 0 \quad (5)$$

has been solved using a method based on the theory of signal flow graph. This method makes it possible to find out the steady concentrations of ions and additionally to evaluate the relative importance of different reactions, whereas it does not give information about the evolution of ions.

The authors of the present paper have developed a method suitable for modeling the ion evolution and the steady state [10]. The next section gives a short summary of the method.

1.2. The computation method for the evolution of ions and the steady state according to the paper [10]

Assuming that matrix A of the problem (1) is constant, the solution of the problem (4) can be written as

$$Y = Y_0 e^{At}, \quad (6)$$

where Y_0 is the vector of initial concentrations. It is reasonable to choose Y_0 to be parallel with vector Q . The solution method of the problem (4), using the peculiarities of the shape of solution (6) has been elaborated in [12].

The solution (6) corresponds to real processes as far as the recombination has not become important, i.e. up to an age of ions of about 10 s, but this fact does not hinder the use of the solution (6) in the computation of the steady state.

Having solved the problem of modeling the ageing of ions (4), we will deal with the problem of the steady state (5). The concentration of small ions corresponding to the steady state n_{st} is constant and can be found from the equation

$$q = an^2_{st} + \beta Zn_{st}, \quad (7)$$

where $q = \sum q_j$ is the summary rate of ion generation.

In accordance to the equation (3)

$$n_{st} = \sum y_{j,st}. \quad (8)$$

Thus in the steady state matrix B (see equation 2) is also constant.

According to equations (1) and (5)

$$AY_{st} - B_{st}Y_{st} + Q = 0 \quad (9)$$

and

$$Y_{st} = (B_{st} - A)^{-1}Q. \quad (10)$$

In principle the steady concentrations of ions could be found by the formula (10), but first, the finding of the inverse matrix in the case of a stiff system may be complicated and second, the finding of a large inverse matrix is time consuming.

The paper [10] presents and proves another possibility of finding the steady concentration. As we already have the solution in the shape (6), we are looking for steady concentrations in the shape

$$Y_{st} = Q_0 \int \frac{Y}{|Y_0|} e^{-B_{st}t} dt, \quad (11)$$

where Q_0 is the matrix whose elements are determined by the formula

$$q_{0,jk} = \delta_{jk}q,$$

Y is the solution (6),

$|Y_0| = \sum y_{0,j}$ is the norm of vector Y_0 .

In paper [10] the identity of equations (10) and (11) has been proved (we will not repeat the proof here).

Matrix B_{st} is to be computed according to equations (2) and (7), i.e.

$$b_{st,jk} = \delta_{jk}(\beta Z + [(\beta Z)^2 + 4aq]^{1/2})/2 \equiv \delta_{jk}b_{st} \quad (12)$$

The computation is organized as follows. First the solution (6) is found and it is obtained in the shape of the table $(t_j; y_{k,j})$. Then equation (13) is used for the approximate computation of the integral (11):

$$y_{st,k} = \frac{q}{|Y_0|} \sum_{j=1}^{n_0-1} \frac{t_{j+1}-t_j}{2} (y_{k,j} e^{-b_{st}t_j} + y_{k,j+1} e^{-b_{st}t_{j+1}}) \quad (13)$$

where $k = 1, \dots, N_0$ (N_0 is the number of concentrations),

n_0 is the number of the points where the solution (6) has been found.

If the solution (6) is found, then the time spent for the solution of the problem (5) on the basis of equation (11) or (13) is negligible.

1.3. Separation of more important variables.

To decrease the number of differential equations in the system (4) $dY/dt = AY$ before starting to find the solution (6) we separated more important reactions, ions, and neutral compounds before each solution. The procedure of the separation of important data is described in detail in [13]. The set of the obtained important data depends on the concentrations of neutral compounds used in the particular problem. This way it is usually possible to decrease the number of equations two times.

2. Data for the modeling of ion evolution

Data necessary for formulating the problem (1) are the description of ion-molecular reactions, the concentrations of neutral compounds participating in ion-molecular reactions, the vectors of initial ion concentrations Y_0 (equation 6) and the quantities α, β, Z, q (equation 7), characterizing ion formation and recombination.

Preferences among existing data on ion-molecular reactions cannot be made randomly. The preliminary determination of the concentrations of neutral compounds also causes problems, as the concentrations of many compounds are not known. Paper [13] contains a more detailed description of the method of forming the set of ion-molecular reactions, and the concentrations of neutral compounds considered natural in the present paper. Here we will only point out that the model describing the kinetics of positive ions contains 1044 reactions, 198 ions and 131 neutral compounds, and the model for negative ions contains 474 reactions, 143 ions and 106 neutral compounds.

As the shape of the solution (6) does not depend on vector Y_0 , the norm of vector Y_0 can be taken equal to 1. The real concentrations of ions are included in the computation of steady concentrations according to equation (11). The values of elements $Y_{0,j}$ of vector Y_0 are presented in [13].

The intensity of ion generation in natural troposphere (near the ground) is about $q \approx 10 \text{ cm}^{-3}\text{s}^{-1}$. In our studies $q = 14 \text{ cm}^{-3}\text{s}^{-1}$. The value of the coefficient of mutual recombination of small ions is taken to be nearly independent of particular ions, in the troposphere its value would be $\alpha = 1.6 \cdot 10^{-10} \text{ cm}^3\text{s}^{-1}$ [7]. As there are numerous measurement data on the equilibrium concentration of ions in the troposphere (n about a couple of hundred of ions cm^{-3}), the value of the quantity βZ can be estimated by formula (7). In our studies $\beta Z = 0.04 \text{ s}^{-1}$.

3. The evolution of positive ions

The basic diagram of the reactions with positive ions has been presented in Fig. 1. The main routes of the evolution of ions are depicted by the continuous lines, the less important routes by the dashed lines. The term "route" may denote direct or mediated (through ions which have not been mentioned) transformation process.

The formulae surrounded by frames signify final ions, the rest are transitional ions. The formulae of ions which are formed in smaller quantities than the main ions are in brackets (e.g. less CH_3^+ ions are formed than N_4^+ ions).

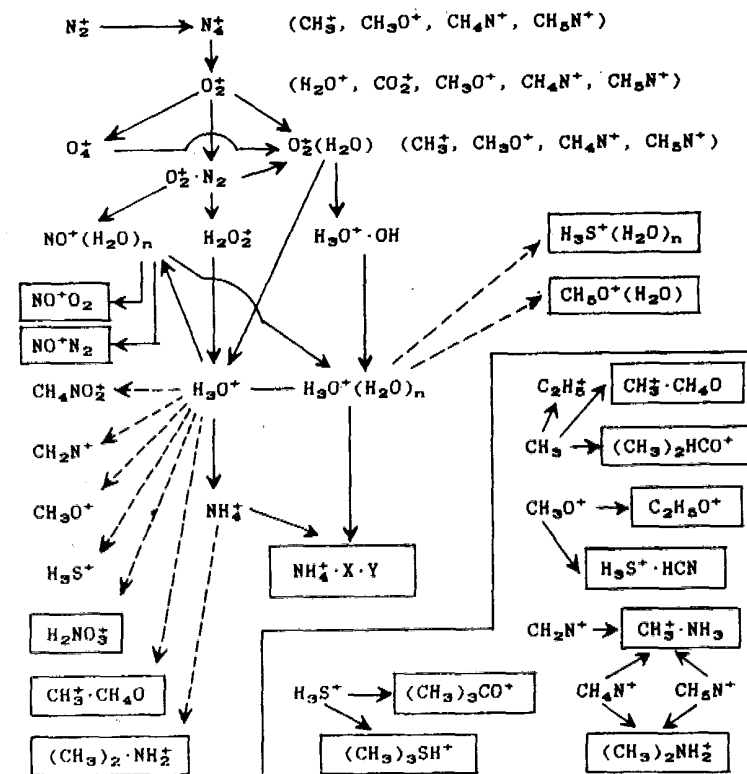


Fig. 1. Diagram of the evolution of positive ions.

3.1. Modeling results for natural concentrations of neutral compounds

The evolution of positive ions during ageing is presented in Fig. 2. The percentages of the dominant ions in the steady state are given in Table 1.

As can be seen in Figs. 1 and 2, the initial ions (mainly N_2^+ and O_2^+) are transformed into the ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$ in 10^{-6} s. The latter achieve their equilibrium concentrations at an age of about 10 μs , and this state remains nearly unchanged up to an age of about 1 s. The final ions start to be formed from the ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$.

The dominance of the ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$ at an age of about 1 μs agrees with experimental results [6].

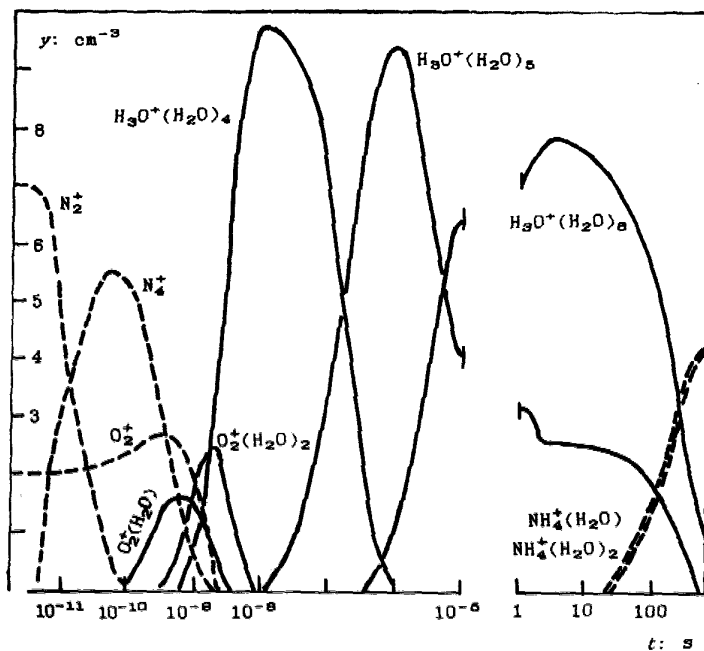


Fig. 2. Time variation of the evolution of positive ions.

According to the modeling results the final ions have cores NH_4^+ . As can be seen from the first column of Table 1, the ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$, and not final ions are dominant in the steady state at natural concentrations of neutral compounds. It is to be pointed out that this does not agree with the measurement results. According to the paper [14] the steady state of the troposphere should not have a significant amount of the ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$. There are two explanations of this discrepancy with the modeling results. First, according to section 3.2. Second, measurement data indicate that alongside with the ions $\text{NH}_4^+ \cdot X \cdot Y$ many other not exactly identified ions are significant in the troposphere. For instance, clusters with pyridine basis are suggested as such unidentified ions in [14]. Due to the absence of data about relevant reactions the formation of such ions cannot be modeled. And in this case, it does not seem necessary to pay too serious attention

to a great number of the ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$ in comparison with empirical data. We will handle this excess as a measure of incompleteness of the present data, the more so because in view of the fact a "correction" of the rate constants of some reactions has made it possible to significantly decrease the number of the ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$.

Table 1
Relative weights of ions in the steady state,
in per cents

$[\text{NH}_3]$ (cm^{-3})	$4 \cdot 10^{11}$	$1 \cdot 10^{11}$	$1 \cdot 10^{12}$	$1 \cdot 10^{13}$
Ions				
$\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$	77	93	56	1
$\text{NH}_4^+ \cdot X \cdot Y$	23	6	43	98

The influence of the variation of some important rate constants on the behaviour of the model deserves a separate treatment. Our experience shows that by relatively small changes of the rate constants of the reactions it is possible to adjust the model in several necessary directions. In the model under discussion we did not use "corrections", mainly for the reason that we do not know all the reactions which make it possible to simulate the formation of all the clusters presented in empirical data.

3.2. The dependence of the evolution on the concentrations of neutral compounds

We have modeled the influence of the changes in the concentrations of the following compounds on the evolution of positive ions: NH_3 , CH_3OH , CH_4 , CH_3NH_2 , CH_3NO_2 , COS , H_2S , SO_2 , $(\text{CH}_3)_2\text{S}$, SF_6 , CH_3SH , C_2HF_6 , CH_2CF_2 , $\text{C}_2\text{H}_3\text{F}$, $\text{C}_2\text{H}_3\text{Cl}$, CH_2F_2 , $\text{C}_2\text{H}_5\text{Cl}$, C_2H_2 , C_2H_4 , C_2H_6 , C_3H_6 , C_3H_8 , N_2O_5 , HCN , C_2N_2 , $\text{C}_2\text{H}_3\text{N}$, NO_2 , $(\text{CH}_3)_2\text{NH}$, H_2O_2 , CH_3COOH , $(\text{CH}_3)_2\text{CO}$, $\text{CH}_3\text{COC}_3\text{H}_7$, CH_3CHO , O_3 . It appears that only the concentration of NH_3 has a strong influence on evolution, whereas a moderate influence is exerted by CH_3OH , CH_4 , CH_3NH_2 , CH_3NO_2 , COS , and H_2S . The change of the concentration of the rest of the compounds by at least 1000 times did not have a significant influence on the evolution of positive ions.

The influence of the change of the concentration of NH_3 is presented in Table 1. If the presumably natural concentration of this compound ($4 \cdot 10^{11} \text{ cm}^{-3}$) is diminished 4 times, then the ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$ become dominant in the steady state. If we increase the concentration 2.5 times, the content of the ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$ in the steady state is roughly equal to the content of final ions $\text{NH}_4^+ \cdot \text{X} \cdot \text{Y}$. If the concentration is further increased, then the ions $\text{NH}_4^+ \cdot \text{X} \cdot \text{Y}$ become dominant instead of the ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$. Thus, if we suppose that the concentration of NH_3 considered natural is too low, and that the concentration of NH_3 should be increased, then the simulation results agree better with experimental results (where the ions $\text{NH}_4^+ \cdot \text{X} \cdot \text{Y}$ are dominant). In this case the modeling results agree with the measurement data according to which the composition of positive ions is independent of the concentration of NH_3 [15]. Indeed, if the concentration of NH_3 exceeds a certain critical limit, then the composition of ions is not influenced any more by the further increase of its concentration.

Due to the influence of the other compounds that have an effect on the evolution of positive ions new final ions are formed instead of the former final ions $\text{NH}_4^+ \cdot \text{X} \cdot \text{Y}$ (see Fig. 1). The reactions of the formation of the new final ions are the slowest in comparison with the reactions of the formation of the ions $\text{NH}_4^+ \cdot \text{X} \cdot \text{Y}$. Thus in the case of a thousandfold increase of all the above compounds, the relative weight of the new final ions will be below 5%.

4. The evolution of negative ions

The general diagram of the reactions taking place with negative ions is significantly more complex than the diagram of the evolution of positive ions. An example of this diagram can be found in [7]. In the case of natural concentration of neutral compounds it is still possible to separate from the general diagram a part depicting the main routes of transformation. This part is depicted in Fig. 3.

The solid lines denote the more important, and the dashed lines the less important transformations. The ions not surrounded with frames are of lesser importance in comparison with the ions surrounded with frames.

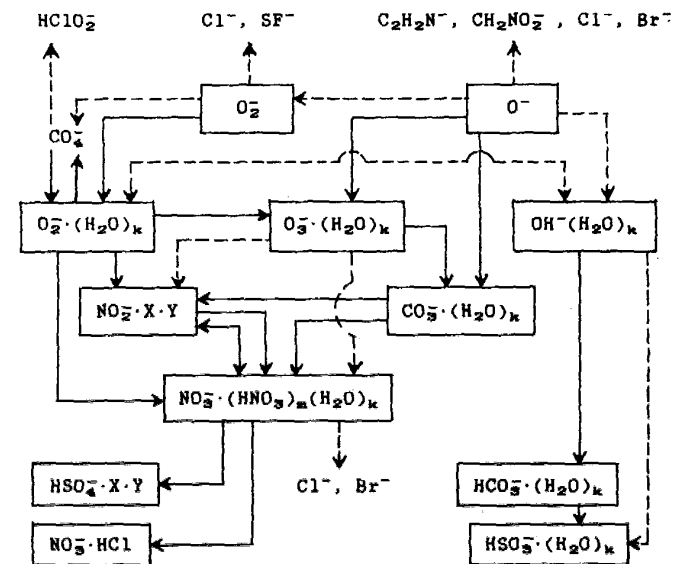


Fig. 3. Diagram of the evolution of negative ions.

4.1. Modeling results for natural concentrations of the neutral compounds

The evolution of negative ions in their ageing is shown in Fig. 4.

The ions $\text{O}_2^-(\text{H}_2\text{O})_k$, $k > 0$ are formed of the initial ions (mostly O_2^-). The former achieve their balanced concentrations at ages below 1 μs . The ions $\text{CO}_3^{2-}(\text{H}_2\text{O})_k$, which in their turn are in balance with the ions $\text{O}_2^-(\text{H}_2\text{O})_k$ are, in the case of a normal concentration of CO_2 , a couple of hundreds of times less numerous than the ions $\text{O}_2^-(\text{H}_2\text{O})_k$. This state is practically unchanged till an age of about 0.1 s, when the formation of the ions of the next stage starts. The result that at an age of about 1 ms the ions $\text{O}_2^-(\text{H}_2\text{O})_k$ are dominant agrees with experimental data. At an age of about 0.1 s the reactions with the participation of

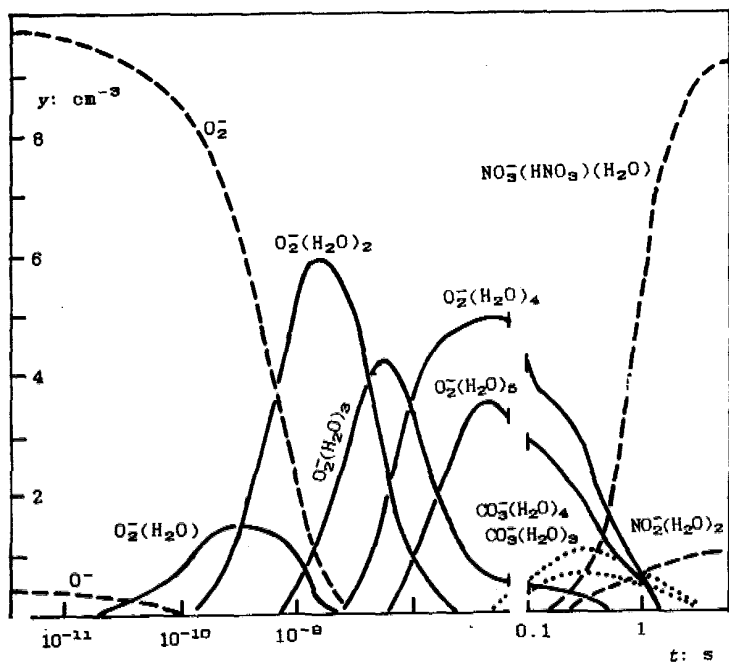


Fig. 4. Time variation of the evolution of negative ions.

three neutral gases become important. First, NO_2 participates mostly in the transformations $\text{O}_2^-(\text{H}_2\text{O})_k \rightarrow \text{NO}_2^-\cdot\text{X}\cdot\text{Y}$. Second, NO participates in the transformations $\text{O}_2^-(\text{H}_2\text{O})_k \rightarrow \rightarrow \text{NO}_3^-\cdot\text{X}\cdot\text{Y}$. Third, ozone participates in the transformations $\text{O}_2^-(\text{H}_2\text{O})_k \rightarrow \text{O}_3^-(\text{H}_2\text{O})_k$. Generally, the final ions $\text{NO}_3^-\cdot\text{X}\cdot\text{Y}$ are formed directly through the chain $\text{O}_2^-(\text{H}_2\text{O})_k \rightarrow \rightarrow \text{NO}_2^-\cdot\text{X}\cdot\text{Y} \rightarrow \rightarrow \text{NO}_3^-\cdot\text{X}\cdot\text{Y}$. However, if the concentration of ozone is sufficiently high, or the concentrations of NO and NO_2 are sufficiently low, the formation of the final ions through the ions $\text{CO}_3^-(\text{H}_2\text{O})_k$ becomes important, whereas the ions $\text{CO}_3^-(\text{H}_2\text{O})_k$ are then formed in a considerable amount.

The ions $\text{NO}_3^-(\text{HNO}_3)_m(\text{H}_2\text{O})_k$ generally do not have the time to be transformed into the ions $\text{HSO}_4^-\cdot\text{X}\cdot\text{Y}$ and $\text{NO}_3^-\cdot\text{HCl}$, i.e. in natural conditions this transformation becomes important not earlier than at an age of a couple of hundreds of seconds. The relative weight of the ions $\text{HCO}_3^-(\text{H}_2\text{O})_k$ will at a normal concentration of water be below 1%.

According to the modeling results, in the steady state of negative ions there are about 85% of the ions $\text{NO}_3^-(\text{HNO}_3)_m(\text{H}_2\text{O})_k$, 10% of the ions $\text{NO}_2^-\cdot\text{X}\cdot\text{Y}$, 2.5% of the ions $\text{O}_2^-(\text{H}_2\text{O})_k$. The result that the ions $\text{NO}_3^-(\text{HNO}_3)_m(\text{H}_2\text{O})_k$ are dominant agrees with experimental data [14]. However, too many $\text{NO}_2^-\cdot\text{X}\cdot\text{Y}$ ions are formed according to the model. In principle, it could be possible to eliminate the discrepancy by changing the rate constants, but as there would be other discrepancies left (as will be explained in section 4.2), we did not worry about the small superfluous part of the ions $\text{NO}_2^-\cdot\text{X}\cdot\text{Y}$.

4.2. The dependence of the evolution on the concentrations of neutral compounds.

In the case of negative air ions the dependence of the evolution on the concentrations of H_2O , O_3 , NO , NO_2 , HNO_3 , SO_2 , H_2SO_4 , N_2O , CH_4 and chlorine compounds has been modeled. The results are presented in the Tables 2 and 3 and in the numbered passages of the following text. State A in Tables 2 and 3 denotes the case where the concentrations of neutral compounds were natural.

1. An increase of the concentration of water shifts the balance of the ions $\text{O}_2^-(\text{H}_2\text{O})_k$ towards larger ions. But as the final ions are formed mostly from the ions $\text{O}_2^-(\text{H}_2\text{O})$ and $\text{O}_2^-(\text{H}_2\text{O})_2$, the formation of the final ions is slowed down. Rows B1 in Tables 2 and 3 present the results for the concentration $4.4 \cdot 10^{17} \text{ cm}^{-3}$.

On the other hand, a decrease of the concentration of water speeds up the formation of the final ions (rows B2, $[\text{H}_2\text{O}] = 1.3 \cdot 10^{17} \text{ cm}^{-3}$).

We can see that the model is rather sensitive to the concentration of water. This result agrees with experimental data [16]. Indeed, on the basis of this paper we can also say that an increase of the concentration of water slows down the formation of the final ions.

2. The concentration of ozone influences the formation of the final ions through the chain $\text{O}_2^-(\text{H}_2\text{O})_k \rightarrow \text{O}_3^-(\text{H}_2\text{O})_k \rightarrow \rightarrow \text{CO}_3^-(\text{H}_2\text{O})_k \rightarrow \rightarrow \text{NO}_3^-(\text{H}_2\text{O})_k$. It appears that this chain is quite important in the formation of the final ions. If we increase the concentration of ozone 4 times in comparison with the normal concentration (rows C1, $[\text{O}_3] = 3 \cdot 10^{12} \text{ cm}^{-3}$), the formation of the final ions is significantly sped up. On the other hand, a tenfold decrease of the concentration

Table 2

The abundances of negative ions (on age of ions 1 s), on various concentrations of neutral gases, in per cents

Ions State*	NO ₃ ⁻ ·	NO ₂ ⁻ (H ₂ O) _k	CO ₃ ⁻ (H ₂ O) _k	NO ₃ HCl	SO ₃ ⁻		
	(HNO ₃) _m ·	O ₂ ⁻ (H ₂ O) _k	HSO ₄ ⁻	Cl ⁻ (H ₂ O) _k	SO ₄ ⁻		
	(H ₂ O) _n ·				NO ₂ ⁻ SO ₂		
A	60	8	13	17	-	-	1
B1	44	4	50	-	-	-	-
B2	86	12	-	0,5	-	-	1
C1	90	2	-	6	-	-	-
C2	14	14	86	-	-	-	-
D1	55	-	20	16	-	-	-
D2	56	44	-	-	-	-	-
D3	68	6	10	10	-	-	-
E1	82	6	12	-	-	-	-
E2	25	10	24	37	-	-	-
F	21	9	18	16	35	-	-
G1	58	8	14	18	-	-	1
G2	58	8	14	18	-	-	1
H1	22	14	16	-	-	-	46
H2	85	6	14	14	-	-	-
L1	37	11	40	11	-	-	1
L2	58	8	14	18	-	-	1
M	21	-	14	17	-	46	1

* The states, presented in Tables 2 and 3, are:

B1 : [H ₂ O] = 4.4 · 10 ¹⁷ cm ⁻³ ;	B2 : [H ₂ O] = 1.3 · 10 ¹⁷ cm ⁻³ ;
C1 : [O ₃] = 3 · 10 ¹² cm ⁻³ ;	C2 : [O ₃] = 8 · 10 ¹⁰ cm ⁻³ ;
D1 : [NO] = 1.6 · 10 ¹⁰ cm ⁻³ ;	[NO ₂] = 2.2 · 10 ⁹ cm ⁻³ ;
D2 : [NO] = 1.6 · 10 ⁸ cm ⁻³ ;	[NO ₂] = 2.2 · 10 ¹¹ cm ⁻³ ;
D3 : [NO] = 1.6 · 10 ¹⁰ cm ⁻³ ;	E1 : [HNO ₃] = 1 · 10 ¹² cm ⁻³ ;
E2 : [HNO ₃] = 1 · 10 ⁸ cm ⁻³ ;	F : [H ₂ SO ₄] = 4 · 10 ¹² cm ⁻³ ;
G1 : [CH ₄] = 3.9 · 10 ¹⁵ cm ⁻³ ;	G2 : [CH ₄] = 3.9 · 10 ¹¹ cm ⁻³ ;
H1 : [SO ₂] = 3 · 10 ¹³ cm ⁻³ ;	H2 : [SO ₂] = 3 · 10 ⁹ cm ⁻³ ;
L1 : [N ₂ O] = 1 · 10 ¹⁵ cm ⁻³ ;	L2 : [N ₂ O] = 1 · 10 ¹¹ cm ⁻³ ;
M : [HCl] = 1.2 · 10 ¹⁴ cm ⁻³ ;	[Cl ₂] = 2 · 10 ¹⁴ cm ⁻³ ;
[HBr] = 4 · 10 ¹¹ cm ⁻³ ;	[Cl] = 4.4 · 10 ¹³ cm ⁻³ .

Table 3

The abundance of negative ions in steady state, on various concentrations of neutral gases, in per cents

Ions State	NO ₃ ⁻ ·	NO ₂ ⁻ (H ₂ O) _k	CO ₃ ⁻ (H ₂ O) _k	NO ₃ HCl	SO ₃ ⁻		
	(HNO ₃) _m ·	O ₂ ⁻ (H ₂ O) _k	HSO ₄ ⁻	Cl ⁻ (H ₂ O) _k	SO ₄ ⁻		
	(H ₂ O) _n ·				NO ₂ ⁻ SO ₂		
A	88	9	2	1	-	-	-
B1	89	5	6	-	-	-	-
B2	91	8	-	-	-	0.5	0.5
C1	95	4	-	1	-	-	-
C2	48	41	10	-	-	1	0.5
D1	94	2	2	1	-	-	-
D2	55	43	1	-	-	1	0.5
D3	88	10	1.5	1	-	-	-
E1	96	3	1	-	-	-	-
E2	74	14	3	5	1	2	0.5
F	19	9	3	1	67	2	-
G1	88	9	2	1	-	-	-
G2	88	9	2	1	-	-	-
H1	44	24	2	-	-	0.5	0.5
H2	87	8	2.5	1	-	-	-
L1	84	11	5	1	-	-	-
L2	88	9	2	1	-	-	-
M	14	-	2	1	-	83	-

of ozone (rows C2, [O₃] = 8 · 10¹⁰ cm⁻³) is accompanied by slowing down of the formation of the final ions. At the same time, in this case more NO₂⁻·X·Y ions are formed, as the transformation process O₂⁻(H₂O)_n → NO₂⁻·X·Y → NO₃⁻·X·Y becomes more important. The influence of ozone on the behaviour of the model is more significant than the influence found in the experiment [15,16].

3. The influence of the concentrations of NO and NO₂ on the evolution of ions is also rather significant. NO mostly influences the rates of the transformations O₂⁻(H₂O)_k → → NO₃⁻·X·Y and CO₃⁻(H₂O)_k → → NO₂⁻·X·Y; NO₂ influences the rates of the transformations O₂⁻(H₂O)_k → → NO₂⁻·X·Y and CO₃⁻(H₂O)_k → → NO₃⁻·X·Y, and also the balance of the ions NO₂⁻·X·Y and NO₃⁻·X·Y.

If we increase $[\text{NO}]$ 10 times and decrease $[\text{NO}_2]$ 10 times ($[\text{NO}] = 1.6 \cdot 10^{10} \text{ cm}^{-3}$, $[\text{NO}_2] = 2.2 \cdot 10^9 \text{ cm}^{-3}$), then in the region of 1 s age ion formation is slowed down, whereas at the same time summarily it is sped up (see rows D1 in Tables 2 and 3). On the other hand, if we decrease $[\text{NO}]$ 10 times and increase $[\text{NO}_2]$ 10 times, then the loss of the ions $\text{O}_2^-(\text{H}_2\text{O})_k$ is sped up, but at the same time a significant amount of the ions $\text{NO}_2^- \cdot \text{X} \cdot \text{Y}$ is formed, as the former balance of the ions $\text{NO}_2^- \cdot \text{X} \cdot \text{Y}$ and $\text{NO}_3^- \cdot \text{X} \cdot \text{Y}$ is shifted.

If we increase only the concentration of NO 10 times, then the evolution of the ions is near to that of the normal state (see Tables 2 and 3, rows D3).

Indeed, the concentration of NO_2 influences the evolution of negative ions also according to the experimental results [15]. At the same time the influence of the concentration of NO should not be noticeable.

4. The concentration of HNO_3 influences the balance of the ions $\text{NO}_3^-(\text{HNO}_3)_m(\text{H}_2\text{O})_n$, and also the formation of these ions of the ions $\text{CO}_3^-(\text{H}_2\text{O})_k$. If $[\text{HNO}_3]$ is higher then the ions $\text{NO}_3^- \cdot \text{X} \cdot \text{Y}$ are larger, which also decreases their transformation into the ions HSO_4^- and $\text{NO}_3^- \cdot \text{HCl}$. If $[\text{HNO}_3]$ is lower, then the ions $\text{NO}_3^- \cdot \text{X} \cdot \text{Y}$ contain more smaller ions, which are capable of being transformed into the ions HSO_4^- and $\text{NO}_3^- \cdot \text{HCl}$.

The concentration of HNO_3 influences mainly the composition of the ions of 1 s age, the influence on the ion composition of the steady state is weaker. Even if we decrease $[\text{HNO}_3]$ a hundred times in comparison with the normal state, the steady state remains relatively unchanged, whereas the part of 1 s final ions is significantly decreased (Tables 2 and 3, rows E2, $[\text{HNO}_3] = 1 \cdot 10^8 \text{ cm}^{-3}$). If we increase the concentration of $[\text{HNO}_3]$ 100 times in comparison with the normal concentration, then the part of the final ions is weakly increased (Tables 2 and 3, rows E1). The fact that the concentration of HNO_3 in general influences the composition of 1 s ions agrees with experimental data [15].

5. Due to the influence of H_2SO_4 , the normal final ions $\text{NO}_3^-(\text{HNO}_3)_m(\text{H}_2\text{O})_n$ are transformed into the ions HSO_4^- . However, the influence of changing the concentration is rather weak. If we want the part of the ions HSO_4^- to become important, it is necessary to increase the concentration 10^4 times (see Tables 2 and 3, rows F, where the concentration of H_2SO_4 is equal to $4 \cdot 10^{12} \text{ cm}^{-3}$).

There are no experimental data confirming the influence of the change of the concentration of H_2SO_4 . On the other hand, it is known that in the steady state of the troposphere, alongside with the ions $\text{NO}_3^- \cdot \text{X} \cdot \text{Y}$, there is a small amount of ions with the core HSO_4^- [3].

6. A hundred-fold change of the concentration of CH_4 did not have a significant influence on the evolution of ions. This agrees with experimental data [15].

7. If the concentration of N_2O is increased a hundred times, then at an age of 1 s there are more $\text{O}_2^-(\text{H}_2\text{O})_k$ ions and less $\text{CO}_3^-(\text{H}_2\text{O})_k$ and $\text{NO}_3^-(\text{HNO}_3)_m(\text{H}_2\text{O})_n$ ions. The steady state remains practically unchanged. A hundred-fold decrease of the concentration of N_2O does not have significant influence on the evolution of ions.

The result agrees with experimental data, where N_2O also belongs to the group of compounds having a weak influence on the evolution of ions [15].

8. Due to the influence of SO_2 the ions $\text{HCO}_3^-(\text{H}_2\text{O})_k$ (there are generally few such ions) are transformed into the ions $\text{HSO}_3^-(\text{H}_2\text{O})_k$, also SO_3^- ions are formed, which can be transformed into the ions $\text{NO}_3^- \cdot \text{X} \cdot \text{Y}$, thus creating one more channel of formation of final ions. The influence of changing the concentration of SO_2 is weak. A decrease of the concentration has practically no influence, whereas a hundredfold increase of the concentration generates a certain amount of SO_3^- ions (Tables 2 and 3, rows H1, $[\text{SO}_2] = 3 \cdot 10^{13} \text{ cm}^{-3}$).

The computational influence of the concentration of SO_2 is weaker than it could be on the basis of the results presented in [15].

9. An at least thousand-fold increase of the concentrations of chlorine compounds (HCl , Cl_2 , freons) has the remarkable influence on the evolution of ions. This result generally agrees with experimental data [15], which predict an extremely strong influence in the case of these compounds, but the influence obtained by computation is too weak.

Conclusions

In the present paper and in papers [8,9] an attempt has been made to compare the behaviour of a model based on chemical kinetics with the measurement data obtained by mass

and mobility spectrometry. The ions of 1 s age and the influence of adding neutral gases to them have been studied only with mobility spectrometry.

Thus, the ions of an age of about 1 ms are similar on the basis of both measurements and modeling. The same (with certain reservations presented in sections 3.1. and 4.1.) is true of the ions of the steady state. However, it is not possible to conclude that the model is sufficiently correct. Namely, certain discrepancies appear between the measurement results and modeling in the case of 1 s ions. First, the influence of many admixtures found to be very important in [15] (HCl, CCl₃COOH, (CH₃)₂NH, CHCl₃, etc.) could not be modeled. Second, the model predicts a strong influence of ozone on the evolution of ions; on the basis of measurements such a strong influence should not exist.

At the same time there are many results coinciding with the measurements of 1 s ions. Indeed, in modeling, as in paper [16], a higher concentration of water slows down the formation of final ions. Indeed, the model is sensitive to the concentration of NO₂ and HNO₃, and weakly sensitive to CH₄ and N₂O in the case of negative ions and to most gases in the case of positive ions.

Finally, we have to point out that though our models have used a relatively large quantity of data and the results agree with relevant measurement results in many respects, a lack of data about several important reactions is still evident.

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