

DISSERTATIONES GEOPHYSICALES UNIVERSITATIS TARTUENSIS

7

**MATHEMATICAL SIMULATION
OF THE EVOLUTION OF AIR IONS**

AARE LUTS

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TARTU UNIVERSITY
PRESS

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LIST OF ORIGINAL PUBLICATIONS

- I Salm, J., and A. Luts, The kinetics of formation of small air ions (in Russian), in *III Vsesojuzn. Simp. po Atm. Elektrichestvu. Tartu, 28–31. okt. 1986. g. Tezisy dokladov*, 48, Tartu, 1986.
- II Tammet, H., J. Salm, T. Parts, A. Luts, Cluster ions in the troposphere (in Russian), in *Fizika Klasterov*, 86, Novosibirsk, 1987.
- III Tammet, H., J. Salm, A. Luts, H. Iher, Mobility spectra of air ions, in *Proc. 8th Int. Conf. on Atmospheric Electricity*, 147, Uppsala, 1988.
- IV Salm, J., A. Luts, The chemical kinetics of tropospheric negative small ions (in Russian), *Acta et Commentat. Univ. Tartu*, 809, 64, 1988.
- V Luts, A., J. Salm, The chemical kinetics of tropospheric positive small ions (in Russian), *Acta et Commentat. Univ. Tartu*, 824, 60, 1988.
- VI Salm, J., A. Luts, A method of computation of steady-state concentrations for a class of problems of chemical kinetics, (in Russian), *Acta et Commentat. Univ. Tartu*, 824, 52, 1988.
- VII Hõrrak, U., H. Tammet, J. Salm, A. Luts, H. Iher, Some results of observation of mobility spectra of tropospheric ions (in Russian), in *IV Vsesojuzn. Simp. po Atm. Elektrichestvu. Nalchik, 7.–11. okt. 1990*, 204, Nalchik, 1990.
- VIII Hõrrak, U., H. Iher, A. Luts, J. Salm, H. Tammet, Mobility spectrum of air ions at observatory Tahkuse, in *Proc. 9th Int. Conf. on Atmospheric Electricity*, 72, St.Petersburg, 1992.
- IX Luts, A., J. Salm, Chemical composition of small air ions in near-ground layer, in *Proc. 9th Int. Conf. on Atmospheric Electricity*, 75, St.Petersburg, 1992.
- X Luts, A., Evolution of small ions at enhanced ionization, in *Proc. 9th Int. Conf. on Atmospheric Electricity*, 532, St.Petersburg, 1992.
- XI Luts, A., J. Salm, Modeling of the evolution of small tropospheric ions, *Acta et Commentat. Univ. Tartu*, 947, 5, 1992.
- XII Luts, A., Chemical kinetics of tropospheric ions at higher ionization rates, *Acta et Commentat. Univ. Tartu*, 950, 39, 1992.
- XIII Luts, A., and J. Salm, Chemical composition of small atmospheric ions near the ground, *J. Geophys. Res.*, 99, 10781, 1994.
- XIV Hõrrak, U., H. Iher, A. Luts, J. Salm, and H. Tammet, Mobility spectrum of air ions at Tahkuse Observatory, *J. Geophys. Res.*, 99, 10697, 1994.
- XV Luts, A., Evolution of negative small ions at enhanced ionization, *J. Geophys. Res.*, 100, 1487, 1995.

1. MATHEMATICAL DESCRIPTION OF THE PROBLEM

1.1. Role of charged particles in the air

The air is a notably complex environment containing hundreds of gases and particles of various types (Junge, 1965; Karol *et al.*, 1983; Batchner and Charlson, 1984). If we took only the weight aspects of the air into consideration, we would confine ourselves to the study of a very limited number of compounds of the air. Any investigation of the processes, specially the chemical processes, proceeding in the air shows the great importance of many various gases and particles which can be characterized by relatively low abundances but also by a considerable activity. A survey of electrically neutral gases found in the air will be given in Chapter 3. In addition to the gases mentioned last, the air contains different particles of various sizes, the total mass of all particles is about a few dozen milligrams per cubic metre (Kikas *et al.*, 1990; Kikas *et al.*, 1992). The particles can be charged or not, in this work we will deal with the small charged particles or small ions. The definition of small ions will be specified in the Article 1.2.

The charged particles of the atmosphere have thoroughly been investigated since the beginning of this century, the early works have been reviewed in detail by (Israël, 1970). According to the earlier concepts, the evolution of atmospheric ions should be viewed as a two-stage process consisting of the arise of ions via ionization followed by the sink of ions via various recombination processes. The concepts of that kind have resulted in contradictions between the assumed ion composition and the observed ion composition. These contradictions have given a rise to new concepts which have started to point out the importance of chemical transformations of ions via ion-molecule reactions (Narcisi, 1966; Danilov, 1968; Fehsenfeld and Ferguson, 1969; Mohnen, 1971; Danilov and Vlassov, 1973). The first works dealing with the transformations of ions mainly concerned the upper levels of the atmosphere. But it was only after the publication of the papers by V.Mohnen in the 1970s, summarized by the survey (Mohnen, 1977), that the new concepts were also applied to the processes taking place in the near-ground atmospheric layers.

In the near-ground air, the charged particles are generated both by the cosmic radiation and by the emissions of radioactive gases (Israël, 1970; Mohnen, 1977; Smirnov, 1980). The steady-state concentrations of the charged particles are determined both by the ionization efficiency, and by the recombination conditions. On the occasion of the approximately natural ionization conditions of the air (up to some tens of ion pairs per cubic centimetre in a second), the total concentration of the small ions of the same sign generally ranges between about 200 and 1500 ions per cubic centimetre (Israël, 1970; Tammet *et al.*, 1992).

Although the concentration of the ions in the near-ground air layer is comparatively low (for example, compared to the concentrations of most neutral gases), the role that the ions play in the air is significant. The atmospheric ions are entirely responsible for electrical conductivity of the atmosphere, in addition they have a certain (up to the present partially unknown) role in the processes of the generation of aerosol, and, consequently, in the formation of precipitations

(Arnold, 1980; Keese and Castleman, 1982; Castleman, 1988; Mohnen, 1990). Additionally, the knowledge about the processes taking place in the course of the evolution of ions have a considerable importance because the composition of ions can be measured more easily than the composition of neutral gases. It is especially the case when the mobility spectrum is used in estimating the composition of ions. Some interesting results obtained by means of the mobility spectrometry imply that in principle the ions could be employed as a very sensitive indicator for the complicated processes taking place in the air (Tammet, 1975; Salm and Matisen, 1977; Iher and Salm, 1982; Parts and Salm, 1992; Parts, 1992). There have been some attempts to realize the potentialities of the atmospheric ion spectrum; the respective method is called "plasma chromatography" (Cohen and Karasek, 1970; Hayhurst *et al.*, 1992). Unfortunately, the actual capabilities of plasma chromatography enable to identify only a few neutral gases under certain conditions. In order to use the atmospheric ion spectrum as an exact and universal indicator for the processes in the air, a sufficiently completed model of the evolution of the atmospheric ions is required. Up to present, no existing model meets the requirements.

The present work has set the following purposes: First, the detailed survey of the current knowledge about the processes of the conversion of ions will be given; secondly, proceeding from the compiled survey, a model will be formed, as adequate to the current knowledge as possible.

1.2. Problem of the specification of a "small ion"

As regards the charged particles (otherwise called "ions") occurring in air, they can have various masses, ranging from electrons to large aerosol particles. There is no universal definition for the term "small ions". Sometimes, small ions are determined either as ions having electrical mobilities of about $1.0 \text{ cm}^2/(\text{V}\cdot\text{s})$ (Israël, 1970) or as ions with a mobility from $0.5 \text{ cm}^2/(\text{V}\cdot\text{s})$ to $2.5 \text{ cm}^2/(\text{V}\cdot\text{s})$ (Salm, 1993). At times, the region of small ions is divided into subregions, e.g. from $0.5 \text{ cm}^2/(\text{V}\cdot\text{s})$ to $1.4 \text{ cm}^2/(\text{V}\cdot\text{s})$, or over $1.4 \text{ cm}^2/(\text{V}\cdot\text{s})$ (Cabane and Milani, 1983). In some works, the region of small ions mentioned above is restricted from below: the ions having a mobility of about $0.5 \text{ cm}^2/(\text{V}\cdot\text{s})$ are considered specific ions, called "intermediate ions" (Tammet *et al.*, 1992). On the substance, the small ions are often identified with cluster ions (Salm, 1993), but such a consideration seems to be valid only in case we treat the ions with the mobility of about $0.5 \text{ cm}^2/(\text{V}\cdot\text{s})$ or less differently from the rest of the ions located in the region of the small ions. As to the majority of the small ions (the ions with an electrical mobility of about $1.0 \text{ cm}^2/(\text{V}\cdot\text{s})$ or more), the mass of a respective ion should be as big as 400 a.m.u. (Kilpatrick, 1971). The ions with a similar mass are indeed typical cluster ions, the evolution of which can be described by means of ion-molecule reactions, on the one hand, and by means of the recombination processes embracing the air ions, on the other hand. As regards the ions with a mobility of about $0.5 \text{ cm}^2/(\text{V}\cdot\text{s})$, masses of such ions should be over 1000 a.m.u. An ion having so high mass can not be considered cluster ion because the evolution of an ion of this type can not be described by means of the ion-molecule reactions.

As regards the problems of specification of a small ion, it is essential to point out that actually, the relation between the mobility of an ion and the mass of the ion can not be exactly determined. In principle, the mobility of an ion depends both on the nature of the ion and on the parameters of the environment. At certain approximations the mobilities of air ions can be calculated by means of the Equation (1.1) (McDaniel and Mason, 1973; Freeman and Armstrong, 1985; Salm, 1993; Tammet, 1995):

$$k = \frac{3}{16} \frac{q}{N} \frac{1}{\Omega} \sqrt{\frac{1}{m} + \frac{1}{M}} \sqrt{\frac{2\pi}{kT}}, \quad (1.1)$$

where k is the mobility of the ion, q is the charge of the ion, N is the concentration of environmental gas, m is the mass of the ion, M is the mass of the molecules of the environmental gas, T is the temperature, and Ω characterizes cross sections of collisions between the ions and the molecules of the environmental gas (collision integral). Nevertheless, the practical employment of the Equation (1.1) leads to considerable complications. Therefore, in case of many problems, specially in case of estimates, various types of semiempirical

$$m = \frac{800}{(0,3 + k)^3} \quad (1.2)$$

equations are preferred, such as the Equation (1.2), obtained by (Tammet, 1992) on the ground of the data reported by (Kilpatrick, 1971). The Equation (1.2) is also used in the present work to obtain the estimates concerning the relations between the masses and the mobilities of ions. Still, some other relations between the masses and the mobilities, different from the one determined by the Equation (1.2) have also been reported, e.g. relations presented in the paper (Cabane and Milani, 1983) result in the masses about twice as big as those obtained by virtue of the Equation (1.2). The mass-mobility relationship reported by (Huertas *et al.*, 1974) is similar to the relation determined by the Equation (1.2) as long as the ions with masses over about 100 a.m.u. are concerned. The former differ from the latter, resulting in the masses exceeding the ones obtained by the Equation (1.2) as soon as dealing with the smaller ions. In the present work we prefer the relation determined by the Equation (1.2) because, on the one hand, the Equation (1.2) has been obtained on the ground of the analysis of a large amount of data reported by (Kilpatrick, 1971), and, on the other hand, a great number of results reported by many other works are often close to the results obtainable via the Equation (1.2) (Mohnen, 1977; Meyerott *et al.*, 1980; Salm, 1992). Additionally, the results obtainable by virtue of the Equation (1.2) are close to the ones obtainable on the ground of theoretical considerations (Tammet, 1995). Moreover, there could obviously be named no other equation comparable to the Equation (1.2) both in simpleness and in yielding the results remarkable for their accuracy. Nevertheless, as for some certain ions, the connections between the masses and mobilities of the ions can differ from the one determined by the Equation (1.2). As the mobility of an ion depends both on the type of an ion and on the environment, under some certain conditions the mobilities can obtain

unusual values which could be observed, e.g., in the papers (Keesee and Castleman, 1985; Salm, 1992; Salm, 1993). Thus, as regards the common cases, the Equation (1.2) can be applied, still, the potentialities of some particular cases should be remembered as well.

Hence, proceeding from the Equation (1.2) the cluster ions should be characterized by mobilities of about $1.0 \text{ cm}^2/(\text{V}\cdot\text{s})$ or more. Proceeding from some another mass-mobility relationship different from the one determined by the Equation (1.2), the region of cluster ions becomes smaller than the region determined by means of the Equation (1.2); e.g. proceeding from the paper (Cabane and Milani, 1983) yields the region of cluster ions characterized by mobilities approximately down to $1.5 \text{ cm}^2/(\text{V}\cdot\text{s})$ since the ion-molecule reactions enable to determine only the transformations of ions having masses up to 400–500 a.m.u.; the transformations of heavier ions can not be determined this way.

In the present work the “small ions” could be defined as the charged particles transformations of which in the air can be determined by the use of ion-molecule reactions (which is equal to the concept of cluster ions). As regards the masses, the corresponding particles can have masses approximately up to 400 a.m.u., as to the mobilities, the corresponding mobilities should be approximately down to $1 \text{ cm}^2/(\text{V}\cdot\text{s})$.

1.3. Mathematical description of the processes involving air ions

1.3.1. Description of an individual ion-molecule reaction

Ions arise by virtue of various ionization processes. The newly arised ions start to participate in ion-molecule reactions, converting the preliminary ions into the ions of other types (Huertas and Fontan, 1975; Mohnen, 1977; Huertas *et al.*, 1978; Basseur and Chatel, 1983; Kawamoto and Ogawa, 1986). As regards the troposphere, both the second-order and the third-order reactions take place:



and



where A^+ , C^+ , E^+ and G^+ are certain types of ions (equivalent to the ions A^- , C^- , E^- and G^- in case dealing with the negative ions, e.g the ions N_2^+ or O_2^-); B , D , F and M are certain neutral gases, whereas M is often called the “third body”, and this component, as a rule, does not change in the course of reaction, the only purpose of it is to participate in stabilizing of the process. The rates of reactions (1.3) and (1.4) can not generally be determined by virtue of any common rule (Atkins, 1986). Nevertheless, all of the known works treating the models of the evolution of ions have considered the rates of ion-molecule reactions (1.3) and (1.4) to be determinable by virtue of the Equations (1.5) and (1.6):

$$d[C^+]/dt = k_1 \cdot [A^+] \cdot [B] \quad (1.5)$$

and

$$d[G^+]/dt = k_2 \cdot [E^+] \cdot [F] \cdot [M], \quad (1.6)$$

whereas $d[C^+]/dt = -d[A^+]/dt = -d[B]/dt$, and $d[G^+]/dt = -d[E^+]/dt = -d[F]/dt$; $[C^+]$, $[A^+]$, $[G^+]$ and $[E^+]$ are the concentrations of the respective ion types; $[B]$, $[F]$ and $[M]$ are the concentrations of the respective neutral gases; k_1 and k_2 are the rate constants of the respective ion-molecule reactions (the problems concerning the data about ion-molecule reactions will be discussed further in Chapter 2). The Equations (1.5) and (1.6) can not be regarded as the common rules, nevertheless, they are valid for a large number of reactions. The Equations (1.5) and (1.6) determine the changes of the concentrations of the respective ion types relative to the concrete ion-molecule reaction, with regard to the reaction (1.3) or (1.4) respectively. In case the ions of a certain type participate in several ion-molecule reactions, we have to write out one equation for each reaction occurring in the system, the equation (1.5) or (1.6) respectively. As regards the changes of the concentrations of ions, the summary change of the concentration for this concrete type of ions can be found by means of adding up all changes determined from the individual equations (1.5) or (1.6).

As it can be seen from the Equations (1.5) and (1.6), an ion-molecule reaction causes a change both in the concentrations of ions and in the concentrations of neutral compounds participating in the ion-molecule reaction. Taking this into account, it would be correct to compile the equations analogical to the equations (1.5) or (1.6) not only for ions, but also for neutral gases. Unfortunately, it would result in serious additional complications as shown below. For that reason, the works dealing with the mathematical simulation of the evolution of ions have not ordinarily taken the potentiality of the changes of concentrations of neutral gases into account: the concentrations of neutral gases are usually considered to be constant (Huertas *et al.*, 1978; Wisenberg and Kockarts, 1980; Brasseur and Chatel, 1983; Lifshitz *et al.*, 1984; Kawamoto and Ogawa, 1986). This simplification can be motivated by the considerations described next. First, as it can be seen from Chapter 3, and from Article 1.1, the concentrations of tropospheric ions are in the most cases at least 10^6 times lower as compared with the concentrations of neutral compounds considered to be natural. Consequently, as far as the ionization efficiency does not much exceed the natural values, proceeding from the ion-molecule reactions can not cause any significant change in the concentrations of the greater part of neutral gases. Thus, confining ourselves to the approximation described last, the concentrations of neutral gases can be considered to be constant. Secondly, we have to consider the situations characterized by the increased ionization efficiency which can not be excluded in general case. The situations of that kind can not be found in the natural air, but they can be met in the limited regions where, because of either natural or artificial conditions, the rate of ion generation is substantially increased. However, such situations can be regarded as the very special cases, in consequence of which it is not necessary to include them into the common model. Such situations can be considered separately, as it will be shown in Article 1.7 Besides, as it can be seen in Chapter 2, the present knowledge about the data about the ion-molecule reactions is quite limited. The lack of information can result in the considerable inaccuracy of the model. Moreover, as it can be seen from Chapter 3, the actual concentrations of several neutral gases have not exactly been determined. Therefore, at the present an estimate is a maximum that can be set as a purpose

in case of dealing with the mathematical simulation of the evolution of ions. As dealing with an estimate, it does not seem expedient to include the reactions between the neutral compounds into the common model. Besides, it would result in the considerable complications with respect to the computations according to the model as it will be shown below. Thus, in the present work, alike in the most of the analogical works, the concentrations of neutral gases are considered to be constant. This is a simplification, indeed, but it can be well motivated, at least in case of natural ionization rates.

1.3.2. Processes of ion generation and recombination

Besides the transformations via ion-molecule reactions, air ions take part in two additional processes: first, the ions arise through ionization processes; secondly, the ions disappear in the course of the recombination processes in the air.

The generation of the ions of a certain type can be characterized by means of the constant q_i , characteristic of the type of ions:

$$dn_i/dt = q_i \quad (1.7)$$

The constant depends both on the conditions of ionization and on the actual concentrations of the neutral gases in the environment under ionization, but does not depend on the concentrations of ions.

The recombination processes concerning small air ions can be, in certain approximation, described by means of Equation (1.8):

$$dn_i/dt = \alpha \cdot n^2 + \beta \cdot n \cdot Z. \quad (1.8)$$

The Equation (1.8) contains some essential simplifications as described in a more detailed form below. Provisionally, we will confine ourselves to the fact that dn_i/dt is the rate of change of the concentrations of a particular type of ions, whereas the change is caused by the recombination processes; $n = n(t)$ is the summary concentration of ions of the same sign, which can be reached after summing up the concentrations of ions of the same sign: $n(t) = \sum n_i(t)$; Z is the summary concentration of the particles of the air characterized by masses significantly greater than those of the small ions. These particles are also called aerosols hereafter; β is the effective coefficient of the rate of the attachment of ions to aerosol particles; and α the coefficient characterizing the rate of the recombination of small ions with the small ions of an opposite sign, in other words, the coefficient of mutual recombination.

Proceeding from the Equations (1.7) ja (1.8), the summary concentration of ions of the same sign n can be found out by means of the Equation (1.9):

$$q = \alpha \cdot n^2 + \beta \cdot n \cdot Z, \quad (1.9)$$

where q is the summary rate of the generation of ions of the same sign: $q = \sum q_i$.

Next, we will present a more detailed description of the simplifications found in the Equations (1.8) and (1.9). First, the Equations (1.8) and (1.9) contain a presumption about the equality of the summary concentrations of ions of opposite signs. As a matter of fact, the summary concentration of positive ions exceeds the summary concentration of negative ions for about 15%, whereas in

some rare cases the difference of about 2 times has been observed (Retalis Dimitris, 1977; Kolokolov *et al.*, 1980; Tammet *et al.*, 1992). However, the presumption about the equality of the summary concentrations of ions of opposite signs has been used very often, which may be motivated by several facts. First, the presumption mentioned last has no direct effect on the composition of ions obtained by means of the model. As a matter of fact, the variations in the summary concentration of ions affect the composition of ions as well, causing a change in the mean lifetime of ions. A similar effect can be obtained by means of a simple change in the value of n in the Equation (1.8). Therefore, an addition of a special member considering the differences between the summary concentrations of the ions of opposite signs into the Equation (1.8) would not create any new quality with respect to the mathematical model considering the processes of recombination. Moreover, the presumption about the equality of the summary concentrations of ions of opposite signs makes the mathematical treatment of the problem easier. And so, as the effects caused by the differences between the summary concentrations of ions can be simulated in an easier way, the presumption mentioned above is employed in most of the works concerning the models of the evolution of ions (e.g. Wisenberg and Kockarts, 1980; Brasseur and Chatel, 1983; Kawamoto and Ogawa, 1986; Arijs, 1992).

Going on with the description of the simplifications contained in Equations (1.8) and (1.9), a second observation could be brought out. According to the Equations (1.8) and (1.9), the rates of recombination should be same for all ion types. Actually, the recombination rate of a certain type of ions depends both on the type of ions, and on the environment. Consequently, the rate must be different for different ion pairs (Bates, 1985b; Gringel *et al.*, 1978). Still, proceeding from the data available the dependence of the rate on the type of ions is not very essential (Keese and Castleman, 1985).

The fact mentioned last is also confirmed by the results obtained by virtue of the calculations in which the averaged parameters were used: the calculated value of the coefficient α was close to the values obtained via various measurements (Bates, 1985b). Although, the coefficient of the mutual recombination depends on the density of the environment as well (Lee and Johnsen, 1989), at the levels from the ground to about 10 km the value of the coefficient of the mutual recombination, α , can be considered to be nearly equal to $1.6 \times 10^{-6} \text{ cm}^3 \text{ s}^{-1}$ (Smirnov, 1980; Bates, 1985b).

The next simplification found in Equations (1.8) and (1.9) would be the fact that the effective coefficient of the attachment of ions to aerosol particles (β) can not actually be regarded as a constant: it depends on the actual aerosol spectrum. The value of coefficient β grows along with the size of aerosol particles (Gringel *et al.*, 1978). On the other hand, the effect of the growth of β on the recombination process is still limited because about 99% of the whole aerosol concentration is usually located in the region of small particles the diameter of which ranges between $0.01 \mu\text{m}$ and $0.18 \mu\text{m}$ (Kikas *et al.*, 1990; Kikas *et al.*, 1992). Inside the limits of the region mentioned above the distribution of the aerosol may be different. This causes a remarkable variation in the value of β ,

whereas in different aerosol situations coefficient β may differ even up to 10 times.

Nevertheless, with respect to the present problem, i.e. with respect to the mathematical simulation of the evolution of ions, the possible variations of the value of β do not require any special consideration. The variations of the value of β directly change the rate of the recombination, resulting in a change of the mean lifetime of ions, which can result in certain variations of the composition of ions because at different ages the ions can be composited differently. All the same, no direct effect of the actual value of β on the composition of ions can not be pointed out, as there are no works available considering β significantly dependant on the type of ions. Hence, the actual values of β can be different in different situations, but the same can be said about the values of Z . Thus, with respect to Equation (1.8) and to the mean lifetime of ions, β and the concentration of aerosol Z can be considered to be equivalent quantities. Taking that into account, we can fix an average value of β , and henceforth, both the variations of the mean lifetime of ions and the possible accompanied effects (certain variations in the composition of ions) can be simulated by means of variations of the value of Z .

The problem concerning the determination of the mean value of β has been studied in the paper (Salm, 1987), and the value equal to $1.3 \times 10^{-6} \text{ cm}^3 \text{ s}^{-1}$ has been found out. As regards the mean value of Z , in the present work the value of $1.2 \times 10^4 \text{ cm}^{-3}$ is considered normal, whereas the actual values of Z can vary at least 10 times (Kikas *et al.*, 1990; Kikas *et al.*, 1992).

1.3.3. Equation of ion evolution

Writing out Equations (1.5), (1.6), (1.7) and/or (1.8) necessary for all the ions selected, we will obtain a system of differential equations (1.10):

$$dY/dt = AY - BY + Q \quad (1.10)$$

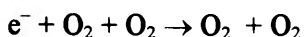
where Y is the vector of ion concentrations, A is the matrix describing the rates of ion-molecule reactions, B is the matrix describing the decay (recombination) of ions, and Q is the vector of the rate of the ion generation determined by virtue of the Equation (1.7). In accordance to the considerations described above, the elements a_{ij} of matrix A are the products of the rate constants of the respective ion-molecule reactions (in case an ion with a type-marker j becomes an ion with a type-marker i); and the concentrations of the neutral compounds participating in the ion-molecule reactions; the elements a_{ij} are to be computed by virtue of Equations (1.5) and (1.6). Taking Equation (1.8) into consideration, the elements b_{ij} of matrix B can be expressed by means of Equation (1.11):

$$b_{ij} = \delta_{ij}(\alpha n + \beta Z). \quad (1.11)$$

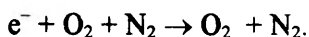
Here, δ_{ij} is the symbol of Kronecker, whereas the meanings of the other members have been defined already in course of the discussion about Equation (1.8).

1.3.4. Problems concerning the composition of primary ions

The elements of the vector Q can formally expressed by virtue of Equation (1.7). In order to determine the content of the elements be q_i , the information about the relative abundances of various types of primary ions generated in the air via ionization processes is required. In course of the primary act of ionization a positive primary ion and an electron are generated. The ionization sources most important in the near-ground layers (cosmic radiation and emission of radioactive elements) have sufficient energy to ionize any molecule. As a result, the relative abundance of positive primary ions in the air is, as the first approximation, determined by the relative abundance of neutral compounds of the air (Israël, 1970; Eisele and Tanner, 1990; Arijs, 1992) (as to the concrete concentrations of neutral compounds, see Chapter 3). Within a few nanoseconds the electrons generated by virtue of the ionization acts react with certain neutral air molecules, resulting in the formation of the ions called negative primary ions. In the main, the ions O_2^- are formed. Generally, the formation takes place by means of reactions



and



In general case, the rates of the reactions mentioned last depend, both on the energy of the electron and on the temperature of the environment. Still, the dependence on the temperature is essential only at a temperature below 250K. As regards the dependence on the energy of electrons, in case of energy with a value from 0.5 eV to 10 eV, the rate constants of the respective reactions do not change more than 2 times, whereas the rate constants have a maximum at about 1 eV. In case the value of energy being below 0.5 eV, a rapid decrease in the rate constants takes place; in case the energy of electrons exceeds a value of about 10 eV, the rate constants are slowly stabilized near the certain value (Caledonia, 1975). Nevertheless, by means of the data reported by (Caledonia, 1975), it is not possible to determine exactly the actual values of the rate constants in case of the energies of electrons being nearly equal to the thermal energies. Presumably, a very rapid decrease in the rate constants starts at a temperature of about 200K.

Besides the ions O_2^- , ions O^- are formed, but under natural conditions the amount of ions O^- is small (Caledonia, 1975; Huertas *et al.*, 1978).

In accordance with some data, e.g. (Huertas and Fontan, 1982; Smirnov, 1980), the composition of primary ions depends both on the composition of neutral environment and on the type of ionization source. Therefore, a special analysis of the composition of primary ions may prove to be necessary. It is particularly the case while using the ionization sources which can not be considered to be natural (e.g., corona discharge), or while studying the processes, the participants of which are very young ions.

Nevertheless, as regards the ages of ions characteristic of natural air, it seems as if the problems of composition of primary ions can be disregarded: in this case the composition of primary ions can most likely be considered independent of the

type of ionization. The judgement mentioned last can be motivated by the results reported by several works, in which some special studies about the dependence of composition of ions on the type of ionization were carried out; the results have shown the composition of ions practically independent of the type of ionization source (Iher and Salm, 1981; Salm and Iher, 1983). In the paper (Huertas and Fontan, 1982) two ionization sources, corona discharge and α -radioactivity, were used: at an age of about some milliseconds, the composition of positive ions has shown no dependence on the type of ionization, but in case of the composition of negative ions a certain dependence was observed. As regards the positive ions, the results mentioned last were also confirmed by the results of the paper (Dzidic *et al.*, 1976), and partially by the paper (Carroll *et al.*, 1975). The results of the paper mentioned last have shown no dependence in case corona discharge or ^{63}Ni -source are used, whereas using the electrons with an energy of about 20eV resulted in some differences in the composition of ions. As to the case mentioned last, the results of such kind may have been caused not by the new type of ionization source but by the accompanied effects: the electrons having so high energies may dissociate the neutral molecules, and thereby, change the actual composition of neutral environment.

As to the negative ions obtained by (Huertas and Fontan, 1982) in case of α -radiation, similar ions have been observed also by the paper (Karasek, 1974). As regards the dependence of the composition of negative ions on the type of ionization source obtained by the paper (Huertas and Fontan, 1982), similar effects can also be explained not by means of the differences of the ionization sources but by means of the changes in the composition of neutral environment, whereas the changes in the composition of neutral environment may not be connected with the change of the ionization source. It can be seen from the paper (Mohnen *et al.*, 1980), that if the concentration of NO_x grows, the ions determined in case of α -radiation in the paper (Huertas and Fontan, 1982) may become the ions determined in case of corona discharge by the same paper. Moreover, corona discharge may indeed generate an additional amount of NO_x molecules. Thus, the differences in the composition of ions obtained by (Huertas and Fontan, 1982) may actually have been caused by the variations in composition of neutral environment, which, in its turn, may partially result from the corona discharge. Probably, the actual extent of variations in the composition of neutral environment depends on the characteristics of corona discharge, as corona discharge was also used in the paper (Iher and Salm, 1981), but no differences in the composition of ions were observed.

Proceeding from the considerations mentioned above, it seems as if the type of ionization source does not have any direct significant effect on the composition of air ions; this judgement is also supported by several papers, e.g. (Hayhurst *et al.*, 1992). In addition, in the papers (Eisele, 1989a; Eisele, 1989b) the composition of ions near high-voltage transmission lines has been studied: the results show the composition of ions dependent on the state of transmission line, whereas the dependence is stronger in case of negative ions and weaker when positive ions are concerned. Nevertheless, the effects observed have been explained not by means of the influence of ionization source on the composition of primary ions, but by means of the changes in other factors. Namely, corona discharge generates not

only ions but also several new types of neutral molecules, which are often in an excited state, and having an increased chemical activity. As to a change in the composition of neutral gases, it will, without doubt, result in a certain change of the composition of ions as well. Hence, at least one part of the obtained variations in the composition of ions can be explained by means of the variations in the composition of neutral gases. Besides, the summary concentration of ions near transmission lines exceeds the concentration of ions in the natural environment. In accordance with the Equation (1.8), the rate of the decay of ions near transmission lines consequently exceeds the rate of the decay of natural ions, resulting in the mean lifetime of ions shorter as compared with the lifetime of natural ions. As regards the mean lifetime of ions, its variations may indeed have certain effects on the composition of ions: the composition of ions may depend on the age of ions, and as a result, a change in the mean lifetime of ions may cause a certain change in the steady-state composition of ions.

Thus, the actual dependence of the composition of ions on the type of ionization seems to be quite negligible. In case of positive ions, the most likely reason for this presumption should be connected with the ion-molecule reactions transforming almost any ions generated by virtue of the act of ionization into a certain composition of new ions which can be considered new primary ions. The processes leading to the new primary ions should terminate within a few nanoseconds (Huertas and Fontan, 1975). As regards negative ions, the negative primary ions originate from of the electrons generated by virtue of the act of ionization. In case the environment contains a considerable quantity of O_2 , the electrons are mainly transformed into the ions O_2^- (Caledonia, 1975). The situation may not be valid in case of the energies of electrons considerably out of the ordinary; this case results in very low values of the rate constants of the reactions leading to the formation of the ions O_2^- (Caledonia, 1975). Naturally, the composition of the primary ions will also be different from that under the natural conditions in case characterized by very low concentrations of O_2 . Nevertheless, neither of the two situations mentioned last can occur in the natural air. As to the works reporting the composition of ions dependent on the type of ionization source, the actual reason for the effects is most likely connected either with the variations in the composition of neutral environment, or with the variations in the mean lifetime of ions. Nevertheless, both of the effects can, at least partially, be due to the ionization source, and particularly depend on the efficiency of the ionization source (Hayhurst *et al.*, 1992; Eisele, 1989a; Eisele, 1989b).

Most of the works dealing with the simulation of the evolution of ions have not proceeded from the charged particles aroused by the act of ionization. Instead, certain fast ion-molecule reactions transforming the preliminary particles into the certain composition of ions have been taken into account, but not included into the common model. The new composition of ions can now be considered to be the primary one. The method described is valid if the processes taking place within the first nanoseconds after the primary act of ionization are not of interest, and if the composition of the neutral environment is not very different from the natural composition. In case the presumptions are met, the method can be considered useful as it makes the model more simple; it results in

the following composition of ions, called the composition of primary ions: 5% O^- , 95% O_2 , 64% N_2^+ , 21% O_2^+ , 6% N^+ , 5% NO^+ , 3% O^+ ja 1% Ar^+ (Lifshitz *et al.*, 1983; Lifshitz *et al.*, 1984; Huertas and Fontan, 1975; Huertas *et al.*, 1978). As regards the remainder components of vector Q according to Equation (1.7), these components are considered to be equal to zero. In order to determine the vector Q completely, the value of the summary rate of ion generation is also required. In case of near-ground air, the value is about tens of ion-pairs per cubic centimetre in a second, whereas the inside rate of ion generation exceeds the outside one (Smirnov, 1980). In the present work we consider the value of 14 pairs of ions $cm^{-3}s^{-1}$ normal, vector Q is determined in accordance with the per cents listed above.

1.4. Survey of the solutions to the evolution equation

A solution to the equation of evolution of ions (1.10) results either in the time changes of the concentrations $n_i(t)$ or, in a particular case (1.12)

$$(B_{st} - A)Y_{st} = Q, \quad (1.12)$$

in the steady-state concentrations of ions $n_i = n_{i,st}$. Following the simplifications described in Articles 1.3.1 to 1.3.4, we obtain both matrix A and vector Q to be constant, whereas matrix B depends on time (in accordance with Equation (1.11), for concentration n depends on time). As regards the steady-state problem (1.12), the time-dependence of matrix B can also be eliminated, as the summary concentration of ions is equal to the steady-state value, $n = n_{st}$, whereas the steady-state value can be found out by means of Equation (1.9). Thus, following the simplifications described above, problem (1.12) can be turned into the system of linear equations with matrix $B = B_{st}$.

As it will be shown below, problem (1.10) has also been converted into a linear problem. This can be done only due to the simplification which considers the concentrations of neutral gases to be constant. Without the simplification mentioned last we would have to deal with the nonlinear problem, whereas a solution of nonlinear equations is much more complicated than that of linear ones.

In the present case, a solution to problems (1.10) and (1.12) is still complicated because of the factors listed as follows:

1) The systems of Equations (1.10), (1.12) are large, with the number of equations being over 100,

2) The systems of equations are stiff, i.e., the values of the members of the equations differ from one another up to 10^{12} times. This makes the employment of any iteration complicated because an iteration step becomes limited to a short timelag determined by the greatest values of the members. Moreover, the requirements to the precision of calculations are also quite strong, as both very rapid and very slow processes must be considered at the same time.

In principle, Equation (1.10) can be solved by means of any method designed for the systems of differential equations, e.g., using the Runge-Kutta method (Levin and Ulm, 1966), which has already been applied in the papers (Huertas and Fontan, 1975; Huertas *et al.*, 1978). Unfortunately, because of the factors

mentioned last, the Runge-Kutta method is applicable only up to an age of ions of some milliseconds, as the integration step can not be increased over some mikroseconds. As to the papers (Huertas and Fontan, 1975; Huertas *et al.*, 1978), the evolution of ions has been considered only up to an age of ions of some milliseconds, owing to which, the problems connected with the integration step were of no importance. As regards the models of the evolution of ions more or less applicable to the natural processes, the models can not be limited to the age of ions of some milliseconds as, in accordance with the considerations described in Article 1.3.2, the actual mean lifetime of small air ions is of 100 orders of magnitude.

Besides the common methods of solution for differential equations, the methods designed specially for the stiff equations are also known, e.g., the Gear method (Gear, 1971), which has been employed in the papers (Lifshitz *et al.*, 1983; Lifshitz *et al.*, 1984). In case of certain problems, the Gear method shows some advantages as compared with the common methods. Nevertheless, as regards the present problem, particularly simulations of the evolution of ions of ages over 1 s, the author of the present work has met certain complications as in certain cases the integration step could not be enlarged because of the limitations connected with the precision of calculations, whereas the limitations of integration step have resulted in the forfeiture of the advantages of the Gear method. On the ground of the information obtained from private communications with the authors of papers (Lifshitz *et al.*, 1983; Lifshitz *et al.*, 1984) the complications mentioned last can be considered to be common. As regards the papers (Lifshitz *et al.*, 1983; Lifshitz *et al.*, 1984), the papers have dealt only with a concrete problem. On that account, the authors of these papers have surmounted the problem by an abundant usage of the computation time. Thus, in case of some problems the Gear method can be considered suitable, nevertheless, as present case contains many problems of different initial data, the Gear method can not be considered to be the most appropriate one.

As to the steady-state problem (1.12), the problem is contained in the system of linear equations, and therefore it can in principle be solved by Equation (1.13)

$$Y_{st} = (B_{st} - A)^{-1}Q. \quad (1.13)$$

Using Equation (1.13), the computation problems are not so serious as compared with the problems described above. Still, it should be taken into account that while the inverse matrix of a large and stiff matrix is being found out, the problems concerning inaccuracy of the computations may arise. As to practice, Equation (1.13) has been employed only by the paper (Brasseur and Chatel, 1983). In several papers (e.g., Wisenberg and Kockarts, 1980; Kawamoto and Ogawa, 1984; Kawamoto and Ogawa, 1986) problem (1.12) has been solved by means of a method called "signal flow graph technique" This method makes it possible to find out not only the steady-state concentrations of ions $y_{i,st}$ but also the relative moments of the concrete ion-molecule reactions. For that reason, the method is more profitable, as compared with the direct application of Equation (1.13).

All the same, problem (1.12) is not the only one worth consideration. Besides the steady-state concentrations of ions obtained while solving problem (12), the results about the time-dependence of the composition of ions are important as well, whereas the results mentioned last can not be obtained by means of the signal flow graph technique. As to the results about the steady-state concentrations of ions, the results make it possible to use one fixed point while comparing the results of simulations with the results obtained by measurements. As it will be shown in Chapter 2, one should not be limited to this fixed point only, as several features of the evolution of ions may appear only at certain ages of ions. Moreover, in addition to the results of the observations of steady-state composition of ions, some results describing the composition of ions at various ages of the ions are available as well, but in case being limited only to the simulation of steady-state the results mentioned last can not be employed. Therefore, in this work we do not confine ourselves to the simulations of the steady-state composition of ions, the simulations of the evolution of ions (the time-dependence of the composition of ions) will also be set as a purpose, owing to which we can not confine ourselves to the methods of solution of problem (1.12). Still, a method similar to the signal flow graph technique can be employed to separate the more essential ion-molecule reactions; the description of the method and the discussions to the point are presented in Article 1.6.

Oftentimes, the methods employed are not completely defined. In that case, compiling of a model and the solution can only be supposed. Various graphical schemes describing the transformation processes of ions have been used in several works, e.g., the very simplified schemes employed in papers (Beig and Chakrabarty, 1987; Beig *et al.*, 1993a; Beig *et al.*, 1993b). In general, the simplified schemes make the recognition of the main features of a model easier, and can therefore be considered useful. Moreover, any simplification decreases the complications connected with the mathematical side of a problem. Unfortunately, oftentimes neither the process of obtaining the schemes nor the methods for a further solution are explained. As to the author of present work, he can not separate the most essential reactions from the set of reactions consisting of thousands of various reactions closely connected with one another, applying the intuitive method only. Hence, the methods employed to obtain the simplified schemes should be introduced before application.

As to the present work, the method used to simplify the model is described in Article 1.6.

In addition to the methods described above, estimates are also widely used in the works dealing with the evolution of ions. Because of the current state of knowledge about the factors, which have an effect to the evolution of ions, estimates are to be considered to be unavoidable. Nevertheless, the possibilities of estimates are quite limited ones, e.g., let us consider the generation of a certain ion. It should be quite attractive to confine ourselves to a few reactions only, e.g., to the reaction generating the ion, and to the one regarded as the main sink of the ion, as it would result in the possibility of a simpler employment of Equations (1.5) and/or (1.6). A method analogical to the one described last will, in this work, be used in case of the analysis of Figure 3.1. Nevertheless, confining ourselves to a few reactions only may result in serious errors, as certain indirect,

and, for that reason, disregarded processes may actually be essential. Thus, estimates are to be considered as such, that is why, no far-reaching conclusions can be done.

In essence, the problems concerning solution to the equations of the evolution of ions are not new, for the analogical problems are also met while dealing with many chemical problems. As a result, some specific mathematical methods are elaborated (e.g., Sild and Palm, 1986). Unfortunately, as regards the early stages of the present work, the method mentioned last has not been completed yet, in consequence of which it was inevitable in the present work to follow another line, as described hereinafter.

1.5. Description of the solution method employed in the present work

In principle, a sub-problem disregarding both process of generation and decay of ions can be separated from the general problem (1.10), the sub-problem can mathematically be expressed by means of Equation (1.14):

$$dY/dt = AY \tag{1.14}$$

Equation (1.14) describes the time-dependencies of the concentrations of ions generated all at once at the initial moment provided that both the ionization and recombination processes would not have any further effect. Equation (1.14) partially simulates the experiment in course of which, at the initial moment, a certain amount of ions is generated, henceforth, the ionization source will be removed and further change in composition of ions will be observed. The experiments like the one described last can really be met, because they result in a solution for problem (1.14) which does not have a mathematical merit only, but possesses certain physical values as well. As regards the practical experiments, recombination processes can not be actually removed. Nevertheless, as long as the age of ions do not exceed the limit at which recombination processes become substantial (under the conditions of natural air: about 10 seconds), the solution $Y = Y(t)$ describes the actual situation comparatively well. Hence, confining ourselves to the ages of ions of about 10 seconds, the problem of simulation of the evolution of ions could be reduced to the solution of problem (1.14), whereas solution to the general problem (1.10) would not be necessary. As to the present work, we do not confine ourselves to the problem mentioned last, the discussion presented above was meant to illuminate the self-dependent physical merit of the solution of Equation (1.14).

In accordance with the simplifications described in Articles from 1.3.1 to 1.3.4, problem (1.14) is a system of linear differential equations with constant coefficients. Therefore, the solution to problem (1.14) can be expressed by means of Equation (1.15):

$$Y = Y_0 e^{At}, \tag{1.15}$$

where Y_0 is the vector of initial concentrations of ions; e^{At} is the exponential matrix. As it becomes evident below, it is reasonable to choose vector Y_0 to be parallel with vector Q , in other words, to choose the initial concentrations of ions $y_{i,0}$ to be proportional with the rates of generation of ions q_i . The easiest way to

obtain the solution to problem (1.14) – (1.15) would be the method elaborated by (Rakitski *et al.*, 1979; Rakitski *et al.*, 1984). In the present work any solution of problem (1.10) is always preceded by the solution to problem (1.14) obtained by means of Equation (1.15), whereas the vector of initial concentrations of ions \mathbf{Y}_0 is determined to be parallel with vector \mathbf{Q} , and vector \mathbf{Q} , in its turn, is determined in accordance with the considerations presented at the end of Article 1.3.4. As it has been mentioned above, the obtainable solution $\mathbf{Y} = \mathbf{Y}(t)$ has a self-dependent merit up to ages of ions of about 10 s, that makes it possible to compare the solution with the available results of measurements, considering the time-changes in the composition of ions. In addition, the solution can be used to obtain the steady-state composition of ions, whereas the steady-state composition can be obtained quite easily. The method employed to obtain the steady-state concentrations has been first introduced by (Salm and Luts, 1988); next section gives a summary of this method.

Let us look for the solution to problem (1.12) in shape (1.16),

$$\mathbf{Y}_{st} = \mathbf{Q}_0 \int_0^{\infty} \frac{\mathbf{Y}}{|\mathbf{Y}_0|} e^{-\mathbf{B}_{st} \cdot t} dt \quad (1.16)$$

where \mathbf{Q}_0 is the matrix, elements of which are determined by Equation (1.17):

$$q_{0,ij} = \delta_{ij} \cdot \sum q_m, \quad (1.17)$$

$\mathbf{Y} = \mathbf{Y}(t)$ is solution (1.15), $|\mathbf{Y}_0|$ is the norm of vector \mathbf{Y}_0 ($|\mathbf{Y}_0| = \sum y_{0,i}$).

Let us prove the identity of Equations (1.13) and (1.16).

Considering Equation (1.15), we can write out:

$$\mathbf{Y}_{st} = \mathbf{Q}_0 \int_0^{\infty} \left(\frac{\mathbf{Y}_0}{|\mathbf{Y}_0|} e^{\mathbf{A} \cdot t} \right) \cdot e^{-\mathbf{B}_{st} \cdot t} dt \quad (1.18)$$

Next, the associativity of the product of matrices and commutativity of matrices \mathbf{A} and \mathbf{B}_{st} are taken use of (matrix \mathbf{B}_{st} is a diagonal matrix), and as a result, Equation (1.18) can be written in shape (1.19):

$$\mathbf{Y}_{st} = \frac{\mathbf{Q}_0}{|\mathbf{Y}_0|} \int_0^{\infty} \mathbf{Y}_0 \cdot e^{(\mathbf{A} - \mathbf{B}_{st}) \cdot t} dt \quad (1.19)$$

The value of the integral in Equation (1.19) can be obtained by, e.g., Newton-Leibnitz formula. As matrix \mathbf{B}_{st} is a diagonal matrix of positive elements, and concentrations $\mathbf{Y}(t)$ obtained by means of Equation (1.15) are definitive because of physical considerations, the integrant approaches zero in case $t \rightarrow \infty$, as it can be seen from Equation (1.16). The same can be said about the derivative of the integrant:

$$\left\{ \mathbf{Y}_0 \cdot (\mathbf{A} - \mathbf{B}_{st})^{-1} \cdot e^{(\mathbf{A} - \mathbf{B}_{st})t} \right\} \rightarrow 0 \quad (1.20)$$

Therefore, the integration results in Equation (1.21)

$$\mathbf{Y}_{st} = \frac{\mathbf{Q}_0}{|\mathbf{Y}_0|} \cdot \mathbf{Y}_0 \cdot (\mathbf{B}_{st} - \mathbf{A})^{-1} \quad (1.21)$$

As the vector of initial concentrations \mathbf{Y}_0 has been chosen to be parallel to the vector of the generation rates of ions \mathbf{Q} as described above, but the elements of diagonal matrix \mathbf{Q}_0 are numerically equal to the summary rate of the generation of ions of the same sign, Equation (1.22) becomes valid

$$\frac{\mathbf{Q}_0}{|\mathbf{Y}_0|} \cdot \mathbf{Y}_0 = \mathbf{Q}, \quad (1.22)$$

and hence, the identity of Equations (1.13) and (1.16) has been proved. The elements of matrix \mathbf{B}_{st} are to be determined according to Equation (1.11), where n is to be considered equal to the summary concentration of the steady-state concentrations of ions with the same sign $n = n_{st}$, in other words, n is to be determined on the ground of Equation (1.9).

The practical calculation on the basis of Equation (1.16) is organized as follows. First, the time-dependence of the concentrations of ions is computed according to Equations (1.14) and (1.15), whereas the results are obtained in the form of the table ($t_i; y_{j,i}$). Next, integral (1.16) is computed approximately by means of trapezium formula, or Equation (1.23):

$$\mathbf{Y}_{st,j} = \frac{q}{|\mathbf{Y}_0|} \sum_{i=1}^{n-1} \frac{t_{i+1} - t_i}{2} \left[y_{j,i} e^{-b_{st} t_i} + y_{j,i+1} e^{-b_{st} t_{i+1}} \right], \quad (1.23)$$

where $j = 1, \dots, N$ (N is the number of various types of ions, i.e., the number of concentrations); n is the number of the points in which the solution (1.15) has been found; t_i are the time coordinates of the points in which the solution (1.15) has been found; $q = \sum q_j$ (the summary rate of the generation of ions of the same sign); b_{st} is numerically equal to a diagonal element of matrix \mathbf{B}_{st} (according to the considerations described above, all the diagonal elements of the matrix are equal between themselves). The practical computations by means of Equations (1.15) and (1.23) have shown the method determined by the equations mentioned last to be the most appropriate to the simulation of the evolution of ions, as compared with the other methods described in Article 1.4. The method enables to obtain both the time-variations of the concentrations of ions and the steady-state concentrations of ions, whereas the obtained solution (1.15) can be used for many times in order to get many steady-state compositions representing the various conditions of ionization and/or recombination. If solution (1.15) is found, the time spent for the computations on the basis of Equation (1.23) will be

negligible. As regards the precision of the steady-state composition obtained this way, mainly, it depends on the step used to find the solution to problem (1.14).

The possible errors can be estimated by means of the comparison between the summary concentration of ions, obtained on the ground of Equation (1.9), and the summary concentration obtained via Equation (1.23). In case the sums mentioned last are different, it means that the integration step, used while solving problem (1.14) was too large. In the present work, the integration step is chosen so that the difference between the two sums would not exceed 1%.

The results obtained by means of the method described above have been published mainly in papers (Luts and Salm, 1992a; Luts and Salm, 1992b; Luts and Salm, 1994).

1.6. Reduction of the number of variables in the equation of ion evolution

In principle, each solution to Equation (1.10) can be preceded by a procedure resulting in the separation of more important reactions. In any particular case, the set of more important reactions may be different because of the different initial data. The results of the procedure may make it possible to remove certain ions from the system, this is in the case when certain ions do not take part in any more important ion-molecule reactions. The removing of some ions from the system is equivalent to a decrease in the number of differential equations in the equation of the evolution of ions. According to the results of experiments carried out by the author of the present work, in this way, it is usually possible to decrease the number of equations at least by a third, at the same time, the correctness of the procedure has been proved as well. As regards the summary economy obtainable by means of the procedure of separation of more important reactions, the storage required can be considerably smaller, whereas the saving in the time spent on computing is not worth mentioning.

The procedure of separation of more important reactions designed by the author of the present work can generally be described as follows:

1) We make comparisons between the rates of ion-molecular reactions proceeding from a concrete ion, i.e. between the rates of the reactions lowering the concentration of the ion. In the first place, we find the quickest irreversible reaction. Next, we compare all the rates of the reactions proceeding from the ion with the rate of the quickest irreversible reaction. The reactions, the rates of which are lower by at least a given number of times, are labelled as unimportant. This process is carried out for all the ions which occur in the system.

2) Next, it is attempted to order the found important reactions into chains (a genetically connected ordering of reactions) starting from the given so-called initial ions. The list of the initial ions can be optional, the list may be equal to the list of the initial ions used by the determination of problem (1.14). Reactions which can not be joined into any chain are labelled. Those reactions are also labelled, which can be ordered into a chain but which, on the assumption that the concentration of the reactant ion is 1, are slower than the given rate limit.

3) All labelled reactions and the compounds not participating in the important reactions are moved away.

The above procedure is illustrated by an example in Figure 1.1.

1) Let us compare the rates of the reactions proceeding from the ion 2. The rate of the reaction $2 \rightarrow 4$ is significantly higher than the rate of the reaction $2 \rightarrow 3$, but the reaction $2 \rightarrow 4$ can not be regarded as the quickest, for it is reversible through the chain $2 \rightarrow 4 \rightarrow 6 \rightarrow 2$. Thus, the reaction $2 \rightarrow 3$ is to be considered the quickest one. As no more reactions proceed from this ion, any unimportant reaction is not labelled here.

Now the rates of the reactions proceeding from ion 4 are compared. The reaction $4 \rightarrow 6$ is reversible, therefore, the reaction $4 \rightarrow 3$ is the quickest. As the reaction $4 \rightarrow 5$ is significantly slower, it can be labelled as unimportant.

Next, let us compare the rates of the reactions proceeding from ion 6. As the both reactions are reversible, the rates are not compared, and unimportant reactions are not labelled.

The analogical procedure is carried out also for the other ions that occur in the system.

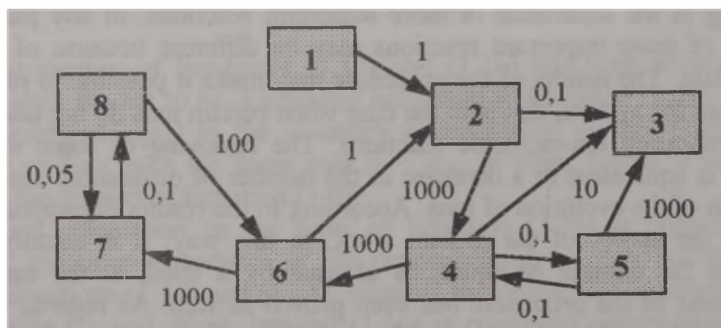


Figure 1.1. Graph of reactions (example). The rectangles denote ions, the arrows denote reactions. The figure at an arrow can be considered to be the rate of the respective transformation.

2) Now we will search for the possible reaction chains between the reactions not labelled yet, starting from the initial ion 1. As the reaction $4 \rightarrow 5$ was labelled as unimportant, then ion 5 is not formed anymore, and the reactions $5 \rightarrow 4$ and $5 \rightarrow 3$ can not be included into any chain. These reactions are labelled additionally. In case the predefined rate limit for the reactions is, e.g. 0.1, the reaction $7 \rightarrow 8$ is slower than this limit. The reaction $7 \rightarrow 8$ can, in principle, be joined into chains, but the reaction is too slow; in this case the reaction $7 \rightarrow 8$ is also labelled.

3) The labelled reactions are moved off. As a result of this, ions 5 and 8 are turned into the not-usable-state, and they are also to be moved off. The procedure described above results in a smaller system: the number of equations is reduced from 8 to 6.

Besides, the procedure described above but modified a little can be used to estimate the relative parts of various transformation processes. This, in its turn, enables to compose the simplified schemes of the evolution of ions. As it has been said above, such schemes are valuable in many aspects. As to the present work, some schemes obtained in this way are presented in Chapter 2.

1.7. Estimate of the concentration changes of neutral gases

As it was said above, the method determined on the ground of Equations (1.14) and (1.16) is valid in case the concentrations of neutral compounds can be considered constant. As regards the natural air, the presumption is appropriate, and the method can be used without any limitation. Nevertheless, the situations characterized by an increased ionization efficiency may be of interest as well. The situations like the one mentioned last can be met in the regions with an extraordinary amount of radioactive substances, and also in the lab instruments in which enhanced ionization is used. As regards the conditions of enhanced ionization, the changes of neutral compounds occurring within ion-molecule reactions can not be disregarded. By means of the linear method described above, the changes of neutral compounds can not be simulated. On the other hand, as it was said in Article 1.4, any nonlinearity should be avoided. Taking this into consideration, an iteration method has been designed in the present work. Any step of the method consists of two stages: first, problem (1.14); (1.16) is usually solved, next, using the found concentrations of the steady state of ions, the changes in the concentrations of neutral compounds are estimated as follows.

Let us have an ion-molecule reaction:



where A^+ and D^+ are ions; B, C, E and F are neutral compounds; the rate constant of the reaction is marked by k .

If the concentration of ions A^+ in the steady state is $[A^+]$, the concentration of compound B changes within 1 s by the value of

$$[B]_{1s} = -k \cdot [A^+] \cdot [B]_0 \cdot [C]_0, \quad (1.25)$$

where $[B]_0$ and $[C]_0$ are the concentrations of neutral compounds B and C which were used for the determination of problem (1.10) on the previous step. Adding up changes $[B]_{1s}$ over all the ion-molecule reactions in the system containing compound B, we obtain the total change of the concentration of compound B within 1 s on the assumption that other concentrations are constant. In this way, the changes of the concentrations of all the neutral compounds participating in ion-molecule reactions can be found out; the changes can be regarded as the next step of the iteration.

If the above iteration is executed for several times, it is possible to estimate both the changes of the neutral compounds and the influence of the concentration change in a certain neutral compound on the ion evolution, and on the concentration change of the neutral compound itself. In principle, the iteration process can be automated, but, unfortunately, the iteration does not converge equally in all cases, whereas some cases of convergences can not be plausible in physical-chemical sense. Thus, the iteration process should be carried out manually; between the iteration steps, trends of convergence should be assessed, and the choice between the different trends of convergence should be done when needed. The result obtained this way can be considered a rough estimate only, but, on the other hand, an estimate is the maximum that can be set as a purpose as far as the model consists only of ion-molecule reactions but of no reactions

between the neutral compounds of the model. If we take into account also the reactions between neutral compounds, the system of Equations (1.10) unavoidably becomes nonlinear, which causes a substantial increase in computational difficulty. Up to now, no successful model consisting of both ion-molecule reactions and the reactions between neutral compounds is known. As regards the estimates, the iteration described above can be regarded as a quite proper one, moreover, the requirement for computation resources is not great.

The results obtained by means of the iteration described above have mainly been published in papers (Luts, 1992a; Luts, 1992b; Luts, 1995).

2. PROCESSES OF THE MUTUAL TRANSFORMATION OF IONS

2.1. Introduction

In this chapter we continue dealing with the problems concerning the determination of matrix **A** in the equation of evolution of ions (1.10). Two types of data will be examined: first, the available data about the rate constants of ion-molecule reactions; secondly, the available data about the actual composition of ions. Particularly, an attempt to analyze the changes in transformation processes caused by variations in pressure and/or temperature will also be made. By means of the results of all these analyses, requirements to the behaviour of the model are set.

In this chapter we are not going deal with the actual concentrations of the neutral compounds, although the concentrations are necessary for determination of matrix **A** as well: the concentrations of the neutral compounds are considered in the next chapter. As to the members of Equation (1.10) which describe generation of ions and/or decay of ions, contents of the members has been analyzed in Article 1.3.

2.2. Survey of the models of ion evolution

In the paper (Ferguson and Arnold, 1981) a qualitative survey both of the formation and the composition of stratospheric ions has been given. The authors of the paper have analyzed the rates of certain ion-molecule reactions, on the ground of which a conclusion about the central role of ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$ in the evolution of positive ions has been done. Ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$ are formed in any case, moreover, several other ions, among the ones arisen from the water by means of the reactions with gases of high proton affinities, become also converted into ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$. In the paper (Ferguson and Arnold, 1981) only two types of ions capable of substituting ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$ have been found out: at the older ages of ions, ions $\text{NH}_4^+(\text{H}_2\text{O})_k$ and/or $\text{CH}_3^+(\text{H}_2\text{O})$ (the ions formed with the help of CH_3OH) may become dominant. However, the principled possibility of formation of certain additional ions, substituting $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$ ions, e.g. ions $\text{Na}^+(\text{H}_2\text{O})_k$, because of the large proton affinity of NaOH , has also been pointed out. The results obtained by means of the analyze of ion-molecule reactions have been compared with some results of measurements. These results have shown proton hydrates (ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$) to be dominant at higher altitudes, whereas a decrease in altitude causes proton hydrates to be less abundant: at lower altitudes the ions of other types are generally dominant.

The main negative ions should be ions $\text{NO}_3^- \cdot \text{X} \cdot \text{Y}$ (Ferguson and Arnold, 1981). In accordance with the discussed set of ion-molecule reactions, formation of $\text{NO}_3^- \cdot \text{X} \cdot \text{Y}$ ions is directly supported by large concentrations of HNO_3 , N_2O_5 and O_3 , at which NO and NO_2 directly conduce the formation of ions $\text{NO}_2^- \cdot \text{X} \cdot \text{Y}$, the contribution to the formation of ions $\text{NO}_3^- \cdot \text{X} \cdot \text{Y}$ is only oblique. In conformity with the set of reactions, most of ions of other types should sooner or later be transformed into ions $\text{NO}_3^- \cdot \text{X} \cdot \text{Y}$, whereas ions $\text{NO}_3^- \cdot \text{X} \cdot \text{Y}$ should be transformed into the shape $\text{NO}_3^- \cdot (\text{HNO}_3)_k$ by sufficient abundance of HNO_3 . The ions

mentioned last can be substituted only by ions $\text{HSO}_4^- \cdot \text{X} \cdot \text{Y}$, abundance of which depends mainly on the concentration of H_2SO_4 . Therefore, ions $\text{HSO}_4^- \cdot \text{X} \cdot \text{Y}$ can be considered the terminal negative ions (Ferguson and Arnold, 1981). The discussion summarized above has been confirmed by some results of measurements: the main ions observed in stratosphere are indeed ions $\text{NO}_3^- \cdot (\text{HNO}_3)_k$, and ions $\text{HSO}_4^- \cdot (\text{HNO}_3)_k \cdot (\text{H}_2\text{SO}_4)_m$, and relative abundances of the ions depend on the altitude and on other conditions.

In the paper (Thomas, 1983) a qualitative survey regarding the available data about evolution of ions at the altitudes from 10 to 100 km has been given. In conformity with the survey, ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$ should be most important in the evolution of positive ions, whereas at lower levels of the atmosphere ions $\text{H}^+ \cdot \text{X} \cdot (\text{H}_2\text{O})_k$ should also become relevant; X can be, e.g. CH_3CN or CH_3OH . As to negative ions, the main results reported by (Ferguson and Arnold, 1981) have been confirmed: the most of the negative ions are transformed into ions $\text{NO}_3^- \cdot (\text{HNO}_3)_k \cdot (\text{H}_2\text{O})_k$, at which the water molecules being contained in the ions are gradually substituted by the molecules of HNO_3 . Besides, some other substitutions are also possible, e.g. ions $\text{NO}_3^- \cdot (\text{HNO}_3)_k \cdot (\text{HCl})_k$ can be formed, but only the substitutions leading to ions $\text{HSO}_4^- \cdot (\text{HNO}_3)_k \cdot (\text{H}_2\text{SO}_4)_m$ can be considered terminal. Still, as regards the near-ground air, the abundance of ions $\text{HSO}_4^- \cdot (\text{HNO}_3)_k \cdot (\text{H}_2\text{SO}_4)_m$ should be lower than the abundance of ions $\text{NO}_3^- \cdot (\text{HNO}_3)_k$.

In the paper (Wisemberg and Kockarts, 1980), where the evolution of negative ions has been studied by means of mathematical simulation but disregarding the possible influence of H_2SO_4 , the main ions at altitudes between 50 km and 60 km have been found to be clusters $\text{NO}_3^- \cdot \text{X}$.

In the paper (Arijs, 1992) a qualitative survey of the present knowledge about the composition of stratospheric ions has been given. The important roles of ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$, $\text{O}_2^-(\text{H}_2\text{O})_k$, and $\text{CO}_3^-(\text{H}_2\text{O})_k$ have been pointed out: in accordance with the data available, formation of any terminal ion should proceed through the ions mentioned last. As to evolution of ions, clusters $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$, $\text{O}_2^-(\text{H}_2\text{O})_k$, and $\text{CO}_3^-(\text{H}_2\text{O})_k$ can be considered a buffer of specific character since the rates of formation of terminal ions depend on the internal distribution of the types of clusters mentioned last. If so, the correct model of internal structure of the types of ions is one of the most important parts of the overall model of evolution of ions. Nowadays, the data necessary for the correct simulation of evolution of ions is still insufficient (Arijs, 1992).

One of the first works, considering the evolution of natural ions near ground, is the paper (Mohnen, 1977). In this paper the importance of the atmospheric trace gases has been pointed out: being limited to the "air-like gas mixtures" (mainly N_2 , O_2 , H_2O , CO_2 with few additions) results in the composition of ions, in which ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$, $\text{CO}_4^-(\text{H}_2\text{O})_k$ ja $\text{O}_2^-(\text{H}_2\text{O})_k$ are dominant without exceptions, whereas the actual composition of air ions is somewhat different. In the paper (Mohnen, 1977) a qualitative estimate of the situation has been drawn: $\text{NH}_4^+(\text{NH}_3)_x(\text{H}_2\text{O})_y$, $\text{NO}_2^-(\text{H}_2\text{O})$ and $\text{NO}_2^- \cdot \text{SO}_2$, have been regarded as the main air ions, whereas the shortage of data about ion-molecule reactions has been pointed out.

In the paper (Smirnov, 1980), an acceptable survey of the knowledge both about the results of measurements and about the results obtained by calculations has been compiled. As to positive ions, the importance of ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$ has been pointed out: the ions are formed in any case, whereas at the age of about 1 ms, the ions have already achieved their internal equilibrium, older ions are transformed into the terminal ions.

The papers (Huertas and Fontan, 1975; Huertas *et al.*, 1978) are among the first ones, considering the evolution of ions quantitatively. Evolution of ions has been simulated until the age of about some milliseconds, and using the air-like gas mixture (N_2 , O_2 , H_2O , CO_2 , NO , Ar). As it has been shown in the paper (Mohnen, 1977), confining oneself to an air-like gas mixture like the one used by the papers mentioned above results in the composition of ions different from the natural one. All the same, the results obtainable this way are quite applicable to the description of young ions. In conformity with the paper (Huertas and Fontan, 1975), the main positive ions at a pressure of about 10 mmHg, and at the age of about 6 ms are ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$ ($k = 1, \dots, 7$), whereas under the atmospheric pressure, formation of the ions is terminated at the ages under 1 ms. In conformity with the paper (Huertas *et al.*, 1978), the final composition of negative ions depends on the composition of initial ions. In case of initial ions O_2^- , the main negative ions are $\text{O}_2^-(\text{H}_2\text{O})_k$, in case of initial ions O^- , the main negative ions are $\text{CO}_3^-(\text{H}_2\text{O})_k$, in case of initial ions OH^- , the main negative ions are $\text{HCO}_3^-(\text{H}_2\text{O})_k$, whereas the rate of formation of the negative ions depends on the pressure: under the atmospheric pressure the formation of ions is terminated at the age of about 10 μs . As known from Article 1.3.4, the natural composition of initial ions makes up nearly 5% O^- , 95% O_2^- . Consequently, the main negative ions at the age of about 10 μs should be ions $\text{O}_2^-(\text{H}_2\text{O})_k$.

In the papers (Huertas and Fontan, 1975; Huertas *et al.*, 1978), comparisons between the obtained results of simulations and the reviewed results of measurements have shown a significantly good accordance. In addition, the reported data about internal equilibriums of clusters $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$, $\text{CO}_3^-(\text{H}_2\text{O})_k$, and $\text{O}_2^-(\text{H}_2\text{O})_k$ have a certain independent value as by means of the data formation of the clusters is described up to quite large values of k .

According to the evaluations of the authors of the papers (Huertas and Fontan, 1975; Huertas *et al.*, 1978), the trace gases disregarded in the papers may become essential only in case of older ions, hence, as regards the ages of ions considered in the papers, ions $\text{O}_2^-(\text{H}_2\text{O})_k$ and $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$ should be dominant under almost any atmospheric conditions. Thus, evolution of young ions can be modelled using the simplified mixture of gases only. Henceforth, ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$ have sometimes been found also at the natural age of ions, formation of negative terminal ions seems to proceed faster: ions $\text{O}_2^-(\text{H}_2\text{O})_k$ have not been found at the natural age of ions.

As a matter of fact, the results obtained by (Huertas and Fontan, 1975; Huertas *et al.*, 1978) can be obtained using a more simplified mixture of gases, consisting only of N_2 with a possibly minimal admixture of O_2 and H_2O (Siegel and Fite, 1976). As regards some special cases, the simplifications mentioned above can not be considered valid anymore, e.g. in case of very dry air, where the concentration of CO_2 exceeds that of H_2O (such situations do not occur in

natural air), at the ages of ions being about some milliseconds, the main ions are $\text{CO}_4^-(\text{H}_2\text{O})_k$ (Mohnen, 1972); in other cases some other ions may be prevailing.

In the paper (Watts, 1992), another model regarding the processes proceeding in mobility spectrometer until the age of ions being about 10 ms is reported. In the paper, not the air but an air-like gas mixture similar to the one employed by (Huertas *et al.*, 1978) is used. The quite detailed analysis of the reactions taking place between the young ions is presented. On the other hand, the results reported by the paper (Watts, 1992) substantially differ from the ones reported by other papers: e.g., at the age of ions being about some milliseconds, and at the concentration of water being about 100 ppm, the main ions were O_2^- . For comparison, the results obtained by (Huertas *et al.*, 1978) under nearly similar conditions, have shown the main ions to be $\text{O}_2^-(\text{H}_2\text{O})_k$, whereas ions O_2^- have been transformed into other ions within some tens of nanoseconds. At the same time, the results of simulations obtained by (Watts, 1992) are in ideal accordance with the results of measurements obtained by the same authors in the paper (Hayhurst *et al.*, 1992).

A little improved model has been reported in the papers (Lifshitz *et al.*, 1983; Lifshitz *et al.*, 1984), an attempt to study the older ions has been made. The ions obtained by means of the model were still lighter than the ones observed in the real air.

The results of a thorough simulation of composition of ions have been reported by (Kawamoto and Ogawa, 1984; Kawamoto and Ogawa, 1986). On the one hand, only the steady-state composition of ions has been simulated, on the other hand, the results obtained accord quite well with the observed composition of atmospheric ions. In the paper, possible effects of many trace gases have been taken into account (HCl , HCN , H_2SO_4 , HNO_3 , etc.), likewise, a comparatively large number of ion-molecule reactions (over 100) have been included. According to the results, in the near ground layer ions $\text{NO}_3^-(\text{H}_2\text{O})(\text{HNO}_3)$ should be dominant, whereas other types of ions should be at least 10 times less abundant; from an altitude of about 10 km the main ions should be $\text{NO}_3^-(\text{HNO}_3)_2$. Nevertheless, despite the good accordance with many results of measurements, the model used by (Kawamoto and Ogawa, 1984; Kawamoto and Ogawa, 1986) is not suitable for simulation of temporal variations in the concentrations of ions, as mentioned in Article 2.4.3. Authors of the model have given much attention to the description of equilibria like $\text{NO}_3^-(\text{H}_2\text{O})_k(\text{HNO}_3)_m \leftrightarrow \text{HSO}_4^-(\text{HNO}_3)_k(\text{H}_2\text{SO}_4)_m$, at the same time, few attention has been given to the processes determining the evolution of ions at the age of about 1 s.

The paper (Brasseur and Chatel, 1983), dealing with stratosphere, can be regarded as nearly equal to the papers reviewed last. As to negative ions, an excellent harmony with the results obtained by (Arnold *et al.*, 1982) can be noted: both of the papers show a rapid replacement of ions $\text{NO}_3^-(\text{H}_2\text{O})_k(\text{HNO}_3)_m$ by ions $\text{HSO}_4^-(\text{H}_2\text{O})_k(\text{H}_2\text{SO}_4)_m$, occurring at an altitude of about 32 km. True enough, the replacement can be simulated quite easily: by appropriate choice of shape of the concentration of H_2SO_4 . The main positive ions obtained in the paper (Brasseur and Chatel, 1983) were $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$ and

$\text{H}_3\text{O}^+(\text{CH}_3\text{CN})_m(\text{H}_2\text{O})_k$, whereas at lower altitudes the relative abundance of ions $\text{H}_3\text{O}^+(\text{CH}_3\text{CN})_m(\text{H}_2\text{O})_k$ increases.

In addition, the paper (Brasseur and Chatel, 1983) has pointed out the estimative character of results obtainable by means of available data: the actual values of many required quantities are not known, therefore, certain estimates are to be included in any model.

Additionally, the paper (Brasseur and Chatel, 1983) contains rather comprehensive tables of ion-molecule reactions employed, including quite detailed (partially: estimated) data about internal equilibriums of clusters $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$, $\text{H}_3\text{O}^+(\text{CH}_3\text{CN})_m(\text{H}_2\text{O})_k$, $\text{NO}_3^-(\text{H}_2\text{O})_k(\text{HNO}_3)_m$, and $\text{HSO}_4^-(\text{HNO}_3)_k(\text{H}_2\text{SO}_4)_m$. Some of the data have been reported also by (Huertas and Fontan, 1975; Huertas *et al.*, 1978), whereas the estimates used by the papers mentioned last partially differ from the ones reported by (Brasseur and Chatel, 1983), which points to another problem: certain estimates are unavoidable, but estimates used by different authors may be not the same.

In the papers (Beig and Chakrabarty, 1987; Beig *et al.*, 1993a; Beig *et al.*, 1993b) the problem of compiling of the model of evolution of air ions has been solved in an original way: the authors have declared, that the detailed model can not be realized at the present time anyway, as a result of what the authors have replaced the consideration of numerous processes of transformations of ions by a consideration of few blocks, at which the processes contained in the blocks are not of interest any longer for the authors. In this way, both the internal structure of the types of ions and most of the individual transformation processes of ions have been disregarded, moreover, also the values of quantities describing the transformations between the blocks have mostly been estimated. In case of positive ions, the evolution is now described by three blocks only (initial ions, $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$, and $\text{H}_3\text{O}^+\cdot\text{X}_m(\text{H}_2\text{O})_n$), in case of negative ions the new structure is somewhat more complicated.

Next, the transformations between the blocks have been described by means of one or two conventional "reactions", whereas the values of quantities describing the "reactions" have been determined from the conditions of the best accordance with the reviewed results of measurements. The model has resulted in altitude-variations of the summary concentrations of ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$, $\text{H}_3\text{O}^+\cdot\text{X}_m(\text{H}_2\text{O})_n$, $\text{NO}_3^-\cdot\text{X}\cdot\text{Y}$, and $\text{HSO}_4^-\cdot\text{X}\cdot\text{Y}$, whereas the results obtained by the authors were significantly close to the observed concentrations reviewed by these authors.

The approach used by (Beig and Chakrabarty, 1987; Beig *et al.*, 1993a; Beig *et al.*, 1993b) is certainly interesting and, besides, at least partially, fitted for the purpose. As it is shown in Articles 2.4.1–2.4.7, from a mobility spectrum one can get only the information about the relative abundances of certain types of ions, but the actual abundances of individual ions are not obtainable. Moreover, also the results obtained by mass-spectrometry do not generally include the abundances of individual ions, they only include either the summary concentrations of ions of a certain type or the summary concentrations of ions having a certain core (see Article 2.3.2). Consequently, it may be really expedient to describe the composition of ions not by means of the concentrations of individual ions but by the summary concentrations of certain classes of ions.

On the other hand, as it is shown in Article 2.5.2, evolution of ions actually depends not only on the quantities describing the transformations between certain classes of ions, but also on the internal structure (equilibrium) of certain classes of ions, whereas some peculiarities in internal structures can be well simulated. In case we disregard all the processes determining the internal structure of classes of ions, in some particular cases the obtainable results may seem true, nevertheless a model of such kind would be far from the real processes of evolution of ions. Surely, such model can be easy to fit in the results of measurements, but contents of the new quantities introduced in the course of compiling the model is anything but clear. Moreover, such model accords most likely with the results of measurements in some certain cases only, at which in some other cases the accordance may be really weak.

It seems as if the adequate simulation of internal equilibriums of classes of clusters is a more complicated task as compared with the simulation of relative summary abundances of certain ion types, e.g., the internal structures of certain classes of ions found by means of simulating by (Brasseur and Chatel, 1983) do not accord well with the results of measurements, while, the found summary concentrations accord with the results of measurements far better. The complications can be, at least partially, explained by the dependencies of equilibriums: equilibriums of clusters depend both on the temperature and on the pressure, as it is described in Articles 2.5.3 and 2.5.4, at which both temperature and pressure are quite variable quantities. Besides, equilibriums of clusters depend on the concentration of water, which is also quite variable. On the other hand, the amount of measurement results concerning the dependencies of composition of ions on the temperature or on the pressure or on the concentration of water is also very limited: (e.g., Salm *et al.*, 1992; Salm and Iher, 1983).

In the paper (Parts, 1988) some positive ions, which could be essential at the age of ions being about 1 s were enumerated, e.g. ions $\text{NH}_4^+(\text{H}_2\text{O})_4(\text{H}_2\text{O})_8$ and $\text{H}_3\text{O}^+(\text{H}_2\text{O})_3(\text{H}_2\text{O})_6(\text{H}_2\text{O})_{12}$. Such ions were declared to be the particularly stable ones, besides, masses of the ions were quite close to the masses, supposable on the ground of mobility spectrums of ions at the age of about 1 s. Particularly stable clusters have also been discussed in the papers (Peifer *et al.*, 1989; Wei *et al.*, 1991; Khan, 1994), in which clusters $\text{H}_3\text{O}^+(\text{H}_2\text{O})_{20}$, $\text{H}^+(\text{NH}_3)_{1.6}(\text{H}_2\text{O})_{20}$, $\text{H}_2^+(\text{NH}_3)_8$, $\text{NH}_2^+(\text{NH}_3)_6$, and $\text{H}^+(\text{C}_2\text{H}_5)_3\text{N}_{10}(\text{H}_2\text{O})_{21}$ were mentioned. On the other hand, such clusters have not been obtained either by measurements or by simulations. Moreover, at the present time, no either thermodynamic or kinetic data required for simulating such clusters is known: e.g., clusters $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ can be simulated only up to cluster $\text{H}_3\text{O}^+(\text{H}_2\text{O})_9$ (Kochanski, 1985).

In the paper (Parts, 1988) clusters $\text{H}_3\text{O}^+(\text{H}_2\text{O})_3$ and $\text{H}_3\text{O}^+(\text{H}_2\text{O})_3(\text{H}_2\text{O})_6$ have also been regarded as the particularly stable ones. The thermodynamic data reported by (Kochanski, 1985) show a jump of values in case of $\text{H}_3\text{O}^+(\text{H}_2\text{O})_3$ but this jump is not confirmed by other works. Thus, on the ground of thermodynamic data, hardly a conclusion about the favoured clusters can be made. The actual shape of distribution of clusters $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ depends mainly on the concentration of water, whereas at the concentrations of water near to the normal top of the shape should be located at $n = 4..7$ True, at a certain concentration of water top of the shape can be located in $\text{H}_3\text{O}^+(\text{H}_2\text{O})_3$, but this is

valid only at the certain concentration of water. All the same, some observations have shown the favoured existence of $\text{H}_3\text{O}^+(\text{H}_2\text{O})_3$ (see Article 2.3.2), yet the result has not been confirmed by other observations. Moreover, in the course of measurement process, break-up of clusters may occur, as a result of which the shape of distribution obtained by measurement may actually differ from the natural distribution of ions (Schlager and Arnold, 1986). Consequently, the favoured existence of clusters $\text{H}_3\text{O}^+(\text{H}_2\text{O})_3$ obtained by some authors may actually be due to the break-up processes, therefore reflecting only the stability of clusters relative to the break-up. Thus, at the present time we can not decide, in which extent the particularly stable clusters become apparent in the natural atmosphere.

Hence, this article can be summarized as follows. At the age of ions being about some milliseconds, ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$ and $\text{O}_2^-(\text{H}_2\text{O})_k$ should be dominant, at which the models (Huertas and Fontan, 1975; Huertas *et al.*, 1978) describe the evolution of so young ions significantly well. Exceptions are possible only in special cases: e.g., in case of special conditions of ionization, or in case of situation where the concentrations of neutral gases differ very much from those but natural. The special cases can not occur in the real air, all the same, they can be met in the situations created artificially. Consequently, for the common case, the model should take the possibility of special cases into account as well. The reviewed works have mainly considered the evolution of young ions, as regards the ions at ages near the natural ones, only certain details are available. Nevertheless, according to the reviewed papers, at older ages ions $\text{H}_3\text{O}^+(\text{CH}_3\text{CN})_m(\text{H}_2\text{O})_k$, $\text{NO}_3^-(\text{H}_2\text{O})_k(\text{HNO}_3)_m$, and $\text{HSO}_4^-(\text{HNO}_3)_k(\text{H}_2\text{SO}_4)_m$ should be formed, but some other ions may be added as well.

The possibility of existence of the clusters including a large number of water molecules, e.g. $\text{H}_3\text{O}^+(\text{H}_2\text{O})_{20}$, deserves certain attention. Nevertheless, the quantitative treatment of such clusters is nowadays impossible because of the lack of data. The treatment of evolution of ions focusing the attention on the description not of individual concentrations of ions, but of the summary concentrations of certain ion classes (Beig and Chakrabarty, 1987; Beig *et al.*, 1993a; Beig *et al.*, 1993b) deserves certain attention as well. Indeed, the known results of measurements include mainly not the individual but the summary concentrations. All the same, the internal structure of ion classes should not be disregarded because of the reasons discussed above.

2.3. Survey of results of mass-spectrometric measurements concerning ion composition

Composition of ions has been measured both at the ages of ions being about some milliseconds, and at the ages near the natural ones. In the next article a survey of the works having dealt with the young ions is given.

2.3.1. Survey of the results obtained under artificial conditions

One of the early works where attempts of experimental investigation of composition of ions were made is the paper (Fite and Rutherford, 1964). In the paper "pure" gas mixtures were used, at which the pressure was of about a few

torrs, the ages of ions were about few milliseconds, and an electron gun was used as the ionization source. First, the results obtained imply that the “pure gases” were not actually pure, e.g., in the “pure” oxygen ions OH^- , NO_2^- , and CO_3^- were observed. Besides, the composition of ions in the mixture of “pure” N_2 and O_2 were very close to the composition in the natural laboratory air, in both cases ions NO_2^- and $\text{NO}_2^-(\text{H}_2\text{O})$ were observed. The existence of such ions, moreover, provided that the ions were so young and the pressure was so low, does not accord with results reported in most other works. As, in addition to the ions mentioned above, ions having masses of about 280 a.m.u. were observed as well, the peculiar effects mentioned above can be explained by means of supposition, that the composition of neutral gases was actually out of control, at least far from the “pure” gases. On the other hand, the existence of the effects like those implies, that the knowledge of the actual composition of the environment has the first-rate importance.

Partially, the changes of the composition of neutral gases could be due to the specific features of the ionization source: electron gun could generate a large number of atoms of dissociated oxygen, that is implied by the large abundance of ions O^- observed in case of “pure oxygen”. It is interesting, that an addition of N_2 has resulted in the disappearance of ions O^- , the same has been observed in case normal laboratory air was used. In accordance with the results of the papers (Caledonia, 1975; Wisenberg and Kockarts, 1980), the electrons generated by primary act of ionization, should react both with O_2 and with N_2 , whereas both of the reactions should result in ions O_2^- . The abundant existence of ions O^- could be possible only in case of a large number of either O atoms or O_3 molecules. A plenty of O atoms could be generated by electron gun. In case of the addition of N_2 the abundance of O atoms may be decreased by means of the reactions with the molecules of N_2 , but in that case a large number of O_3 molecules should be generated (Baulch *et al.*, 1980), which, in its turn, should contribute to the generation of ions O^- (Caledonia, 1975; Wisenberg and Kockarts, 1980). Still, in case of addition of N_2 molecules, ions O^- were not observed anymore. Besides, the large quantity of ions O^- may disappear by means of ion-molecule reaction between O^- and N_2 , proceeding from which the large number of ions NO_2^- observed can be explained as well (Albritton, 1978). All the same, by the reaction between O^- and N_2 , the competing reaction between O^- and O_2 should proceed as well, whereas the reaction mentioned last should generate ions O_2^- (Ikezoe *et al.*, 1987), which can surely produce ions O_2^-N_2 , but not ions NO_2^- (Albritton, 1978).

In the paper (Huertas *et al.*, 1974) the compositions of positive air ions under the pressure being between 10 mmHg and 30 mmHg, and at the age of ions being about 1 ms have been measured. Under the pressure equal to 10 mmHg, the main ions were $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$, besides, some other ions, e.g. $\text{O}_2^+(\text{H}_2\text{O})_k$ and NO^+ were observed. At the pressure equal to 30 mmHg, the part of $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$ increased. The results are quite close to those obtained by means of simulation, as it was reviewed in Article 2.2: indeed, among very young ions both ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$ and some other ions should exist, at which ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$ should become dominant from the age of about 1 ms. In addition, in the paper (Huertas *et al.*, 1974) the effects of an increase in the concentrations of several neutral gases on

composition of ions has been studied. According to the paper, ethanol, acetone, and ammonia have had an essential effect. E.g., as a result of an increase in the concentration of ammonia, ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$ were replaced by ions $\text{NH}_4^+(\text{H}_2\text{O})_k(\text{NH}_3)_m$. Smaller effects have been observed due to benzene and some of its derivatives, also due to CH_3NO_2 . Practically no effect has been observed due to CCl_4 . On the one hand, the information about the effects caused by an increase in the concentrations of certain neutral gases is very useful because it illuminates certain new branches of the evolution of ions. On the other hand, no quantitative conclusion can be made because there is no information about the actual concentrations of the neutral gases used.

In the paper (Huertas and Fontan, 1982) the compositions of both positive and negative ions under the pressure of about 30 mmHg, and at the age of ions being about 1 ms have been measured. In case of positive ions, ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$ were dominant, at which the composition of ions did not depend on the nature of ionization source. In case of negative ions, the composition of ions has depended on the nature of ionization source: in case of α -emissions, the main ions were $\text{O}_2^-(\text{H}_2\text{O})_k$, in the same place but in case of corona discharge, $\text{NO}_2^-(\text{H}_2\text{O})_k$ and $\text{NO}_3^-(\text{H}_2\text{O})_k$ prevailed. As shown in Article 2.2, both ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$ and $\text{O}_2^-(\text{H}_2\text{O})_k$ accord with the known models of the evolution of ions. As regards ions $\text{NO}_2^-(\text{H}_2\text{O})_k$ and $\text{NO}_3^-(\text{H}_2\text{O})_k$, particularly in case of young ions, they rather belong to the "special cases". In this "special case", existence of the ions might be due to accompanied effects of corona discharge as it was explained in Article 1.3.4: the corona discharge might cause a change in the composition of neutral gases followed by a change in the composition of ions.

In addition, in the paper (Huertas and Fontan, 1982) the variations in composition of ions due to large increases (about 0.5% per volume) in the concentrations of several neutral gases were studied. According to the results, in case of positive ions, $\text{C}_6\text{H}_5\text{NO}_2$ has induced ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k(\text{C}_6\text{H}_5\text{NO}_2)$; CH_3CHO has induced ions $\text{CH}_3\text{CHOH}^+(\text{H}_2\text{O})_k(\text{CH}_3\text{CHO})$; and $\text{C}_2\text{H}_5\text{COCH}_3$ has had a certain considerable effect as well. At the same time, neither CCl_4 nor C_2HCl_3 had any notable effect. In case of negative ions, $\text{C}_2\text{H}_5\text{OH}$ has induced ions $\text{O}_2^-(\text{H}_2\text{O})_k(\text{C}_2\text{H}_5\text{OH})$; and C_2HCl_3 has induced ions $\text{Cl}^-(\text{H}_2\text{O})_k$.

In case of the natural air, concentrations of the neutral gases mentioned above do not achieve the values equal to 0.5% per volume, or $1.3 \times 10^{17} \text{ cm}^{-3}$. Therefore, we had to make sure whether the neutral gases can or cannot have an influence also on the composition of natural ions as well. According to the results in Chapter 3, actual concentrations of all the compounds of interest are not known. On the other hand, the known concentrations of most trace gases are at least 10^6 times lower as compared with the concentrations used in the paper (Huertas and Fontan, 1982). Consequently, as the normal pressure exceeds the one used in the paper (Huertas and Fontan, 1982) for about 25 times, under natural conditions the reactions leading to the ions observed in that paper should be at least 10^4 times slower. Thus, under natural conditions the effects due to the neutral gases might become apparent from the ages of ions being about 10 seconds. In principle, the reactions may become essential, all the same, the possibility of using them depends on the available data about the characteristics of the reactions.

In the paper (Mohnen, 1972) ions in the “air-like gas mixtures” have been studied. The exact composition of the mixture was not defined, the only information about it was that the concentration of CO_2 exceeded the that of water. Besides, ages of the ions were nearly 10 ms. The main ions in such mixture were $\text{CO}_4^-(\text{H}_2\text{O})_k$, besides, there were a few ions $\text{O}_2^-(\text{H}_2\text{O})_k$. In case of addition of SF_6 (the concentration is unknown), the only ions in the system were ions SF_6 .

In the paper (Mohnen *et al.*, 1980) also the composition of young ions in the not exactly defined air-like gas mixtures was studied. In “normal” case, ions $\text{O}_2^-(\text{H}_2\text{O})_k$, $\text{CO}_4^-(\text{H}_2\text{O})_k$, and $\text{CO}_3^-(\text{H}_2\text{O})_k$ were observed, at which the ratio of the concentration of $\text{O}_2^-(\text{H}_2\text{O})_k$ to the concentration of $\text{CO}_4^-(\text{H}_2\text{O})_k$ depends on the ratio of the concentration of H_2O to that of CO_2 ; $\text{CO}_3^-(\text{H}_2\text{O})_k$ is induced by the reactions including atomic oxygen. In principle, the existence of ions $\text{CO}_3^-(\text{H}_2\text{O})_k$ can indeed be explained by the change in the ionization conditions because the similar ions were also found by means of simulation, in case of primary ion O^- (Huertas *et al.*, 1978). On the other hand, ions $\text{CO}_3^-(\text{H}_2\text{O})_k$ were observed in the paper (Mohnen *et al.*, 1980), but not in the paper (Mohnen, 1972), although the parameters of ionization sources seemed to be the same. As the authors of the paper (Mohnen *et al.*, 1980) have said nothing about that contradiction, it is likely to guess that the “air-like gas mixtures” used in the both papers of the same authors were really different. Besides, the different ages of ions can be supposed as well. Consequently, the actual reason for the contradiction remains unclear.

Besides, according to the paper (Mohnen *et al.*, 1980) an addition of SO_2 induces ions $\text{SO}_4^-(\text{H}_2\text{O})_k$; an increase in the concentration of NO_x induces ions $\text{NO}_2 \cdot \text{X}$; and an addition of both ozone and NO_x induces ions $\text{NO}_3 \cdot \text{X}$. Nevertheless, no quantitative conclusion valid for the model can be done because the conditions used in the paper (Mohnen *et al.*, 1980) were not exactly defined.

In the paper (Arnold *et al.*, 1982) the composition of ions in the air-like gas mixtures was studied. In the mixture consisting of N_2 , O_2 , H_2O , and SO_2 ions $\text{HSO}_4^-(\text{H}_2\text{SO}_4)_k$ were observed, which situation accords with the results of measurements of the same authors. All the same, the ions observed in the paper differ from the ions observed as a result of an addition of SO_2 in the paper (Mohnen *et al.*, 1980), although it seems as if the conditions were similar in both cases. It is possible, that the ages of the ions used in the paper (Arnold *et al.*, 1982) were different from the ones used in the paper (Mohnen *et al.*, 1980), still, the actual reason for the differences remain unclear.

Summarizing the discussion presented in this article, following conclusions can be made. First, the results of measurements of composition of young ions have often shown both observed and simulated compositions to be similar. Consequently, the models reviewed in Article 2.2 can be taken for the basis for a better model. Secondly, processes including several neutral gases, such as SO_2 , NO_x , ozone, ammonia, SF_6 , $\text{C}_6\text{H}_5\text{NO}_2$, CH_3CHO , $\text{C}_2\text{H}_5\text{OH}$, acetone, benzene, C_2HCl_3 should be included into the more complete model. As regards the results showing the effects due to the neutral gases which become apparent already on the occasion of very young ions, no quantitative conclusion valid to the model can be done because the concentrations of the neutral gases having had an effect

on the composition of young ions were extremely large, and, moreover, often not exactly defined. Thus, only the qualitative conclusions considering the potentiality of additional branches of the evolution of ions can be done.

2.3.2. Survey of results obtained in natural air

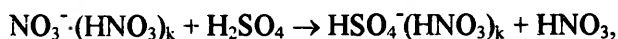
In the papers (Arnold *et al.*, 1981a; Arnold *et al.*, 1981b; Arijs *et al.*, 1982) a survey of results of observations of stratospheric ions is given.

On the one hand, composition of stratospheric ions may differ from that of the near-ground ions. On the other hand, in stratosphere, ions with masses up to about 400 a.m.u. have been found out, but such ions should, in accordance with the discussion presented in Article 1.2, have mobilities close to the mobilities of the ions of the near-ground air (see also Article 2.4). Consequently, stratospheric ions should be similar to the air ions, at least as regards the masses of both ions, therefore, the results obtained for stratosphere, may still be useful.

The composition of positive ions observed at an altitude of about 35 km by (Arnold *et al.*, 1981a) was the following: 21% of $\text{H}_3\text{O}^+(\text{H}_2\text{O})_3$, 20% of $\text{H}_3\text{O}^+(\text{CH}_3\text{CN})(\text{H}_2\text{O})_2$, 18% of $\text{H}_3\text{O}^+(\text{H}_2\text{O})_4$, 16% of $\text{H}_3\text{O}^+(\text{CH}_3\text{CN})_2(\text{H}_2\text{O})$, 11% of $\text{H}_3\text{O}^+(\text{CH}_3\text{CN})_2$, besides, some other clusters of same types. The similar ions have been found out also by (Arijs *et al.*, 1982), at the same, the shape of distribution of clusters was completely different: the main ions were $\text{H}_3\text{O}^+(\text{H}_2\text{O})_3$ (32% – 38%) and $\text{H}_3\text{O}^+(\text{CH}_3\text{CN})(\text{H}_2\text{O})_2$ (30% – 44%), the abundance of other ions was much smaller. Yet, the observed composition of ions may be not equal to the actual composition of ions: the problem of break-up of larger clusters in the course of measurement process has deserved a special attention (Arnold *et al.*, 1981a; Arnold *et al.*, 1982b). As to negative ions, the problems similar to the one mentioned last have been further studied by (Schlager and Arnold, 1986): several clusters observed were indeed most likely to be the products of break-up processes.

The composition of negative ions observed at an altitude of about 36.5 km by (Arnold *et al.*, 1981b) was as follows: 66% of $\text{NO}_3^-(\text{HNO}_3)_2$, 14% of $\text{HSO}_4^-(\text{HNO}_3)_2$, 7% of $\text{HSO}_4^-(\text{H}_2\text{SO}_4)$, 5% of $\text{HSO}_4^-(\text{HNO}_3)$, additionally a few per cents of other clusters with cores of HSO_4^- or NO_3^- . Besides, a special discussion about the role of break-up processes has been carried out: because of the quite high binding energies of negative ions, the observed composition of ions should not differ very much from the actual one, all the same, the real ions containing some molecules of water might disappear within break-up processes.

In the paper (Arnold *et al.*, 1982) study of stratospheric ions was continued with the main attention to the heavier ions. The following ions were observed: $\text{NO}_3^-(\text{HNO}_3)_2$, $\text{HSO}_4^-(\text{HNO}_3)$, $\text{HSO}_4^-(\text{H}_2\text{SO}_4)_3$, $\text{HSO}_4^-(\text{H}_2\text{O})(\text{H}_2\text{SO}_4)_3$, $\text{HSO}_4^-(\text{H}_2\text{SO}_4)_2$, $\text{HSO}_4^-(\text{H}_2\text{SO}_4)$, and $\text{NO}_3^-\cdot\text{HNO}_3$. Various other NO_3^- or HSO_4^- clusters having masses up to 587 a.m.u. were observed as well, still, the abundance of the clusters mentioned last was quite negligible. It is supposed, that at a sufficient concentration of H_2SO_4 , the reaction



always becomes essential, at which the molecules of HNO_3 will be later replaced by the molecules of H_2SO_4 , in summary, both the rate of the processes and the

degree of transformations depend on the actual concentration of H_2SO_4 . Besides, a replacement of ions $\text{NO}_3^-(\text{H}_2\text{O})_k(\text{HNO}_3)_m$ by ions $\text{HSO}_4^-(\text{H}_2\text{O})_k(\text{H}_2\text{SO}_4)_m$ was observed at an altitude of about 30 km: at 32.4 km, about 70% of all the ions had masses below 200 a.m.u., at 34 km, about 70% of all the ions had masses beyond 300 a.m.u. As to the specified values of m and k in groups $\text{NO}_3^-(\text{HNO}_3)_k$ and $\text{HSO}_4^-(\text{H}_2\text{O})_m(\text{H}_2\text{SO}_4)_k$, the specified values could not be obtained because of the possible role of break-up processes. In the paper (Schlager and Arnold, 1986) a further study of the break-up processes was carried out, the suspicions about the essential role of break-up were partially confirmed: the "doubtful" ions of the paper (Arnold *et al.*, 1982) were replaced by ions $\text{HSO}_4^-(\text{H}_2\text{SO}_4)_k$.

In the paper (Arijs *et al.*, 1985) the composition of negative ions at altitudes of 22–45 km has been measured: the main ions were NO_3^- and HSO_4^- clusters, analogically to the results described above, at which the amount of ions $\text{NO}_3^-(\text{HNO}_3)_2$ was about 50% of all the ions.

At altitudes of 52–61 km the main positive ions were $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$, whereas ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_3$ were dominant at 48 km, and ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_2$ at 56 km (Pfeilsticker and Arnold, 1989). The main negative ions at altitudes of 35–55 km were the clusters of NO_3^- and HSO_4^- although somewhat lighter than those at lower altitudes, for ions $\text{NO}_3^-\text{HNO}_3$ and NO_3^- were the main ones, and, besides, CO_3^- clusters and ions NO_3^-HCl were found out (Pfeilsticker and Arnold, 1989).

The first known measurements of ions at altitudes below 10 km belong to the papers (Arnold *et al.*, 1984; Heitmann and Arnold, 1983). In these papers, the mass resolution was quite crude, owing to which the results primarily give the integral information. First, it seems as if the positive ion spectrum depends on altitude, at which a specially large number of heavy ions (with masses up to 500 a.m.u.) appeared at altitudes below 4 km, sometimes, a spectrum containing many heavy ions was observed also at altitudes above 8 km. Secondly, the composition of positive ions seems to be a quite variable one, as different measurements realized at near altitudes have resulted in significantly different spectrums. In the paper (Arnold *et al.*, 1984) no direct conclusion about the composition of positive ions has been done. As regards negative ions, it looks as if the spectrum was somewhat less complicated: the main negative ions at altitudes of about 10 km were NO_3^- and HSO_4^- clusters.

The measurements of near-ground composition of ions started only in the middle of 1980-s, at which in all known works the equipment close to the one described for the first time by (Eisele, 1983) has been employed. The equipment usually works under the conditions where ions sampled from the air pass through a dry buffer gas before being analyzed, as a result, the weakly bound ligands of ions, specially water molecules, boil off, and the observable spectrum looks more simple as compared with the spectrum before buffer gas chamber. Consequently, the spectrum obtained this way is not equal to the natural spectrum, most of all, the final spectrum includes the more stable parts of ions (cores of ions), which is nearly of same contents as the summary concentrations of classes of ions, still, no information about individual ion species can be obtained.

In the paper (Perkins and Eisele, 1984) the first results obtained by means of the equipment mentioned above have been reported. As to positive ions, the particles with masses 54 a.m.u., 72 a.m.u., 90 a.m.u., and 108 a.m.u. were

constantly found, the respective ions were considered to be $\text{NH}_4^+(\text{H}_2\text{O})_k$. Sometimes, a notable amount of particles with masses 60 a.m.u., 78 a.m.u., 80 a.m.u., 94 a.m.u., 98 a.m.u., and 112 a.m.u. were present, at which the particles mentioned last were more frequent at coastal regions, and less frequent on the top of a 1900 m-height mountain. On the other hand, on the top of the mountain, sometimes, quite heavy ions (with masses up to 600 a.m.u.) were observed. None of the last enumerated ions was identified, the ion of 112 a.m.u. was supposed to be the water cluster of the ion of 94 a.m.u., the ion of 78 a.m.u. was supposed to be the water cluster of the ion of 60 a.m.u. Besides, it was mentioned, that an ion with a mass of 60 a.m.u. might contain CH_3CN , but, as an objection to this it was said, that acetonitrile should be an unvariable component of air, whereas the observed concentration of ions with a mass of 60 a.m.u. was actually significantly variable. As to negative ions, only ions $\text{NO}_3^-(\text{H}_2\text{O})_n$ (particles with masses of 62 a.m.u., 80 a.m.u., and 98 a.m.u.), and $\text{NO}_3^-(\text{HNO}_3)$ (mass 125 a.m.u.) were observed, at which ions $\text{NO}_3^-(\text{HNO}_3)$ were dominant. Besides, the possibility of regarding the particles with a mass of 98 a.m.u. as ions $\text{NO}_3 \cdot \text{HCl}$ was also mentioned.

In addition, younger ions have also been studied. To accomplish this, the ions were generated artificially, the ages of the ions were between 0.1 s and a few seconds (Perkins and Eisele, 1984). In case of positive ions, only ions $\text{NH}_4^+(\text{H}_2\text{O})_k$ were observed, therefore, the composition of younger ions was different from the one of natural ions. In case of negative ions, the observed ions were nearly the same as in case of natural ions.

The results of the paper (Eisele and McDaniel, 1986) are similar to the ones of the paper (Perkins and Eisele, 1984). In case of positive ions, ions $\text{NH}_4^+(\text{H}_2\text{O})_k$ were constantly observed, additionally, a smaller portion of particles with a mass of 80 a.m.u. existed almost constantly, likewise variable portions of ions with masses of 60 a.m.u. and 94 a.m.u. were sometimes found. The last three ions mentioned were guessed to be the clusters of trimethylamine, pyridine, and picoline, being based on the quite high proton affinities of the guessed cores of ions. In case of negative ions, ions $\text{NO}_3^-(\text{HNO}_3)_n(\text{H}_2\text{O})_m$ were dominant, in addition, a smaller amount of ions with a mass of 160 a.m.u. was observed, the respective ions were thought to be $\text{NO}_3^-(\text{HNO}_3)(\text{H}_2\text{O})_2$ or $\text{NO}_3^-(\text{HNO}_3) \cdot \text{HCl}$ or $\text{HSO}_4^- \cdot \text{HNO}_3$. Besides, in case of both positive and negative ions some comparatively heavy particles (beyond 200 a.m.u.) were observed, but their nature was not discussed.

In the paper (Eisele, 1986), for the first time, an improved equipment was employed: a collision chamber making a more complete removing of ligands possible has been added. As a result of that, the final spectrum contains only the stable cores of ions, which, in its turn, results in more simple spectrums. In the paper (Eisele, 1986) the main attention has been given to positive ions: the stable cores observed were of 18 a.m.u., 60 a.m.u., 80 a.m.u., 94 a.m.u. and 108 a.m.u., which were identified as ammonia, unknown, pyridine, methylpyridine (or picoline), and dimethylpyridine (or lutidine), respectively.

In the paper (Eisele, 1988), for the first time, a once more improved equipment was employed: the new equipment has made the study of the internal structure of selected ions possible. The supplement enables an improved

identification as now it was possible to cause break-ups of the ions of interest, and this way, getting information about the more stable parts of the ions. In case of positive ions, the stable cores of 60 a.m.u., 80 a.m.u., 94 a.m.u., 108 a.m.u., and 122 a.m.u. were observed constantly, at which sometimes, the cores of 108 a.m.u. were dominant, at other times, the dominant cores were of 80 a.m.u. and 94 a.m.u. In the latter case, the spectrums of positive ions also included a large amount of cores ranging from 170 a.m.u. to 290 a.m.u., whereas in the former cases, the portions of heavy ions were generally negligible, only once a small portion of ions of 222 a.m.u. was observed. A special attention has been given to the particles of 94 a.m.u. and 108 a.m.u., as a result of this, the most likely cores were found to be methylpyridine and ethylpyridine, besides, the supposition about the ions of 80 a.m.u. consisting of pyridine was confirmed. In addition, the ions of 60 a.m.u. are considered to consist of trimethylamine.

In the paper (Eisele, 1988), the spectrums of positive ions at the age of about some hundreds of milliseconds were measured as well. The spectrum of young ions strongly depended on external conditions. Next, we refer to the previous paragraph: in the former case, only the ions of 18 a.m.u., 36 a.m.u., 37 a.m.u., 55 a.m.u., and 80 a.m.u. were observed, the ions were identified as $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$, $\text{NH}_4^+(\text{H}_2\text{O})_k$, and the ions containing pyridine; in the latter case ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$ and $\text{NH}_4^+(\text{H}_2\text{O})_k$ were found as well, in return, also certain heavy ions were already present; the main heavy ions had masses of 130 a.m.u., 172 a.m.u., and 186 a.m.u. Thus, at the age of about some hundreds of milliseconds, ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$ and $\text{NH}_4^+(\text{H}_2\text{O})_k$ are constantly met, but in some circumstances, a large amount of quite heavy ions may be present as well.

The spectrum of negative ions has also been observed: in accordance with the short summary reported in (Eisele, 1988), the whole range between 50 a.m.u. and 150 a.m.u. of the the spectrum was filled out, all the same, the ions with cores NO_3^- , $\text{NO}_3^-(\text{HNO}_3)$ ja HSO_4^- were usually dominant.

In the papers (Eisele, 1989a; Eisele, 1989b), the main attention has been given to the peculiarities of composition of ions due to a near high-voltage transmission line. According to the results, the composition of ions near an energized transmission line is different from the one of natural ions. The equipment used in the paper (Eisele, 1988) was employed again, as a result of which, the results do not generally reflect the actual composition of individual ion species but only the composition of stable cores of ions.

Conformably to the paper (Eisele, 1989a), main cores of natural negative ions were NO_3^- , HSO_4^- , and $\text{C}_3\text{H}_3\text{O}_4^-$ (malonate ion), at which the ions with core NO_3^- were favoured at nights (the ions of 62 a.m.u., 80 a.m.u., and 125 a.m.u), the cores HSO_4^- (mainly ions $\text{HSO}_4^-(\text{H}_2\text{SO}_4)$ with a mass of 195 a.m.u.) were met only in the daytime, yet not constantly; in return, the ions of 195 a.m.u. were sometimes absolutely dominant. A certain number of the ions of 103 a.m.u. and 166 a.m.u. was observed almost all the time, still the ions were favoured in the daytime: the ions were guessed to include $\text{C}_3\text{H}_3\text{O}_4^-$ and $\text{C}_3\text{H}_3\text{O}_4^-(\text{HNO}_3)$. Sometimes, the ions with masses of 113 a.m.u. and/or 176 a.m.u. were observed, the latter one was supposed to be the former one plus HNO_3 , at which the nature of the former remained unclear. Besides, the rarely occurred ions of 142 a.m.u. remained also unknown.

As it was said above, the composition of ions has depends on the state of a transmission line. Near the energized transmission line, the ions with cores NO_3 were constantly dominant, which fact was explained by shorter lifetimes of these ions, that is why the younger ions are more essential. As cores NO_3^- were constantly met, the ions containing $\text{C}_3\text{H}_3\text{O}_4$ were to be found almost all the time, and the ions including HSO_4 were to be met most rarely, the last mentioned ions were supposed to be the oldest ones, with respect to them, the remainder two ions were considered to be intermediate products of evolution of ions.

A few measurements were done by means of the equipment with the collision chamber moved off resulted in the spectrums, which ought to be closer to the natural spectrum of ions. At nights, the ions with core NO_3 , and the unknown ions with a mass of 142 a.m.u. were the most customary ones, while the unknown heavier ions were quite rarely found. The daytime spectrums of negative ions were highly involved; the customary spectrums included both NO_3^- and/or HSO_4 clusters and a large amount of heavy ions with masses up to 400 a.m.u., sometimes up to 700 a.m.u..

In conformity with the paper (Eisele, 1989b), the main positive ions have usually included methylpyridine and/or ethylpyridine (the masses of cores being 94 a.m.u. and 108 a.m.u.), the ions containing either trimethylamine (with a mass of 60 a.m.u.) or quinoline (of 130 a.m.u.) or pyridine (of 80 a.m.u.) were ordinarily less abundant. The ions with the cores of 18 a.m.u., 36 a.m.u., 70 a.m.u., 122 a.m.u., 136 a.m.u., 150 a.m.u., and 164 a.m.u. were also often found, nevertheless, they were more variable. The ions observed as 18 a.m.u. and 36 a.m.u. were most likely NH_4^+ and $\text{NH}_4^+(\text{H}_2\text{O})$. The nature of the ions marked as 70 a.m.u. has remained unclear, all the same, the possibility of isoxazole as one of the components has been mentioned. As regards the other more variable ions, they were thought to include various methyl derivates of pyridine. Sometimes, considerable quantities of ions with masses 186 a.m.u., 196 a.m.u., 202 a.m.u., 204 a.m.u., 217 a.m.u., 218 a.m.u., 232 a.m.u., 258 a.m.u., 260 a.m.u., 270 a.m.u., and/or 274 a.m.u. were observed. Generally, the ions enumerated last have remained unknown, only the ions 202 a.m.u. and 204 a.m.u. were thought to contain a certain kind of amine.

The composition of ions has depended on the state of transmission line. Near the energized transmission line, the ions containing ammonia were more abundant, far from the transmission line often the unknown heavy ions became apparent. The mentioned effect was explained by means of the differences in the lifetimes of ions: the lifetimes of ions near transmission line should be shorter, owing to which, the younger ions become dominant. As to the ions including ammonia, they were regarded as the younger ones, the other ions observed in the spectrum of natural ions were thought to originate from the ions including ammonia. Besides, the portion of ions containing pyridine did not sink below 50%.

In the paper (Eisele and Tanner, 1990), the identification of tropospheric ions was continued. The main positive ions were again found to be the ions containing either pyridine or a certain derivate of pyridine, and ions $\text{NH}_4^+(\text{H}_2\text{O})_k$. The other positive ions were less abundant. The observed spectrum of positive ions did not show any clear diurnal variation, in return, the spectrum had a dependence both

on the individual place of measurements and on the season of the year. Often, ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$ have occupied about 10% of all the spectrum, sometimes the very variable ions with masses of 60 a.m.u. and/or 70 a.m.u. were also present. The former was thought to include trimethylamine, the latter was thought to contain isoxazole. Additionally, sometimes the ions with masses of 90 a.m.u., 130 a.m.u., and/or 144 a.m.u. were met, ordinarily these ions had a small abundance. The first one was thought to contain either dimethylethanol or sacrosine; the second one, quinoline; the third one, methylquinoline. In late spring, the ions with masses of 182 a.m.u., 196 a.m.u., 210 a.m.u., and/or 224 a.m.u. became apparent, the ions were thought to be conditioned by vegetation, containing of glyucose together with some amines was supposed. At times, the ions with masses of 110 a.m.u. and 112 a.m.u. were observed, the ions were thought to be due to winds from the industrial areas.

The main negative ions observed in the paper (Eisele and Tanner, 1990) were the ions containing NO_3^- , HSO_4^- and/or $\text{NO}_3^-(\text{HNO}_3)$, while the composition of negative ions has shown a diurnal variation: the ions including HSO_4^- were more abundant in the daytime, specially on sunny days; the fact was explained by means of the dependence of the concentration of H_2SO_4 on radiation of the sun. Sometimes ions with masses of 142 a.m.u. and/or 158 a.m.u. were also met, the ions were thought to be SO_4NO_2^- and SO_4NO_3^- .

In the paper (Tanner and Eisele, 1991), certain masses unknown up to now were identified. The very variable ions with a mass of 60 a.m.u. were guessed to contain trimethylamine ($(\text{CH}_3)_3\text{N}$), the ions with masses of 74 a.m.u. isobutylamine, the ions of 114 a.m.u. caprolactam, the ions of 130 a.m.u. and 144 a.m.u. quinoline and methylquinoline. All the ions enumerated above in this paragraph were, as a rule, substantially less abundant than either the ions including pyridine or ions $\text{NH}_4^+(\text{H}_2\text{O})_k$. Sometimes, only the ions containing pyridine and ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$ became apparent, which situations were explained by low concentrations of ammonia.

The spectrum of negative ions observed in the paper (Tanner and Eisele, 1991) was again quite complicated. The main cores of negative ions had masses of 62 a.m.u., 95 a.m.u., 97 a.m.u., and/or 103 a.m.u. Besides, the cores with a mass of 95 a.m.u. were also identified: the ions were guessed to be the CH_3SO_3^- . The spectrum of negative ions showed a considerable diurnal variation: the ions including NO_3^- were nearly constant, whereas in the daytime the relative abundance of ions HSO_4^- increased, and at nights the ions including CH_3SO_3^- were more abundant. Sometimes, a considerable number of ions containing $\text{C}_3\text{H}_3\text{O}_4^-$ became apparent, all the same, abundance of the ions mentioned last highly depended on the place of measurements, and, in ordinary case, it was low.

The results reviewed in this article can shortly be summarized as follows.

In the first place, the results obtained by means of mass-spectromeric measurements do not generally include any information about individual ion species, only the shape of distribution of more stable parts of ions (cores of ions) can be obtained, which is nearly similar to the distribution of the summary concentrations of classes of ions in content.

It seems as if the composition of negative ions is relatively more simple, as in this case the similar ions have been observed both in stratosphere and in the

near-ground air. In ordinary case, the ions containing NO_3^- and/or HSO_4^- are met, at which the most common individual ion species are thought to include $\text{NO}_3^-(\text{HNO}_3)_2$ and $\text{HSO}_4^-(\text{HNO}_3)_2$. As to the ions at the ages below 1 s, the ions including NO_3^- are usually dominant. The cores of ions are surrounded by different molecules, first of all, by water, HNO_3 , and/or H_2SO_4 , at which both the size and the individual composition of clusterized molecules depend on the altitude and, similarly, on the actual concentrations of neutral gases. Up to now, actual compositions of individual clusterized molecules of the air are not well-known. Additionally, different other near-ground ions can be found as well, e.g. the ions nowadays thought to include $\text{C}_3\text{H}_3\text{O}_4^-$, CH_3SO_3^- , SO_4NO_2^- , and SO_4NO_3^- . Sometimes, the ions containing $\text{NO}_3^-(\text{HCl})$ are also mentioned. The composition of negative ions shows a clear diurnal variation: at nights, the abundance of ions including HSO_4^- is quite low. As regards the actual masses of negative air ions, sometimes they can reach values from 400 a.m.u. to 700 a.m.u. According to Equation (1.2), the respective mobilities should be about $0.95 \text{ cm}^2/(\text{V}\cdot\text{s})$ and $0.75 \text{ cm}^2/(\text{V}\cdot\text{s})$, which mobilities accord with the results reviewed in Articles 2.4.4, 2.4.7, on the condition, that the heaviest ions were not very frequent.

Spectrum of positive ions seems to be even more involved, and likewise, more dependent on the altitude: at altitudes of about 50 km, the dominant ions are $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$, whereas at altitudes of about 10 km ions with masses up to a few hundred a.m.u. can be met, and near the ground, the masses of positive ions can reach values up to about 600 a.m.u. Near the ground, the most ordinary ions are ions $\text{NH}_4^+(\text{H}_2\text{O})_k$, and/or the ions including either pyridine or its derivatives. Oftentimes, the ions mentioned last are the dominant ones. As to ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$, near the ground they are less abundant, all the same, they can be observed quite frequently: the ions mentioned above are thought to come from ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$. In case of ions at the ages up to a few seconds, the main ions are $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$, $\text{NH}_4^+(\text{H}_2\text{O})_k$, and/or the ions including pyridine, still, at times some quite heavy ions were present as well. Most of the types of positive ions are quite variable, becoming apparent rarely, but in considerable amounts. The variable ions were thought to contain CH_3CN , different amines, glucose, sacrosine, quinoline. Generally, spectrum of positive ions shows both seasonal variation and the dependence on the place of measurements, but shows no clear diurnal variation. On the average, the summertime masses of positive ions exceed the ones in winter. As regards the masses of positive ions, they accord with the estimate obtained by Equation (1.2), and as mentioned in the previous paragraph, on condition that the heaviest ions were not very frequent.

2.4. Survey of the results obtained by the means of mobility spectrometry

2.4.1. Survey of the problems of the interpretation of mobility spectra

As it has been mentioned in Article 1.2, there is no simple nexus between the mass and the mobility of the ion. While not dealing with some specific features, it is most expedient to proceed from a certain empirical formula fitted in environments like the air, e.g., from Equation (1.2). In this way, the calculations

are more simple and the problems connected with correct determination of quantities being contained in theoretical formulas like (1.1) are avoided. In case of employment of Equation (1.2) only the requirement of reduction of measured mobilities to the normal conditions is to be remembered: the mobilities measured under different conditions will be comparable one to another. The reduction of mobilities is based on the fact, that the mobilities are inverse proportional to the density of environment, according to Equation (1.1); the density in its turn is dependent both on the temperature and on the pressure as is generally known. Equation (2.1) enables the reduction of measured mobilities:

$$K_0 = K(T, P) \frac{273,16}{T} \frac{P}{760}, \quad (2.1)$$

where $K(T, P)$ is the measured value of mobility at temperature T and at pressure P (units: mmHg), K_0 is the reduced mobility to be determined (Mohnen, 1977; Meyerott *et al.*, 1980; Salm *et al.*, 1992). Equation (2.1) has been used in many works. As a matter of fact, Equation (2.1) is only an approximation: provided that the difference between temperatures is smaller than 50° , the error of Equation (2.1) should be below 5% (Tammet, 1995).

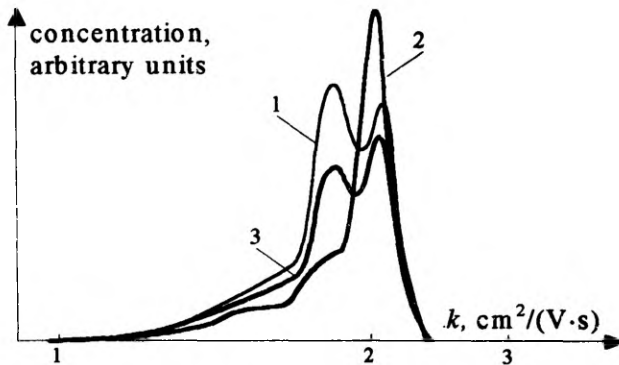


Figure 2.1. Mobility spectrums of negative ions from papers (Iher and Salm, 1981; Salm and Iher, 1983). 1– spectrum at the age of ions of 0.37 s; 2– spectrum at the age of ions of 1.2 s; 3– the same as 2, at increased humidity.

Besides the problems conditioned by undetermination of the connection between mass and mobility, there is at least one other problem that makes interpretation of mobility spectrums more difficult: unlike a mass-spectrum, a mobility spectrum is not a discrete spectrum. Figure 2.1 depicts a few mobility spectrums, that can be regarded as the typical ones. All the peaks of mobility spectrum are characterized by notable widths. The width of the peak of a mobility spectrum is conditioned by several factors: a considerable portion of the summary width is due to specific features of the measurement process (Watts and Wilders, 1992),

in addition, several ions with similar mobilities may actually become apparent in the form of one peak that can not be further resolved in any way. Shapes of mobility spectrum were studied by (Tammet, 1975), it was shown, that the shape of a peak approaches by appropriate composition of ions a certain limit, which can be regarded as the peak of mobility spectrum, at which the limit depends on the certain equipment.

The problems of interpretation due to the final width of a peak are not the last ones. As found out by mass-spectrometric measurements (see survey in Article 2.3), the air ordinarily contains about ten different ion species, at least more than one or two. Therefore, one peak observed in a mobility spectrum does not, at least in general case, correspond to any individual ion. Moreover, the limited number of peaks in a mobility spectrum can not be explained by means of a decrease in a number of peaks due to similar mobilities as mentioned above, for it is no reason to assume, that air ions would always have mobilities very close one to another.

The actual reason for the conflict mentioned in the previous paragraph has been explained by (Mohnen, 1977): a peak of mobility spectrum corresponds not to one individual ion but to one chain of reactions being in its equilibrium.

Let us consider the system, the transformations proceeding in which are graphically depicted in Figure 2.2.

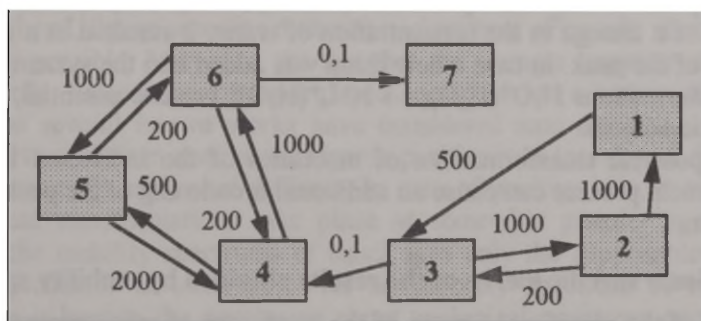


Figure 2.2. Graph of reactions (example). The rectangles denote ions, the arrows denote reactions. The figure at an arrow can be considered to be the rate of the respective transformation.

As we can see in Figure 2.2, the system includes 7 different ion species, at the same, 3 in some respects similar formations can be separated. It is obvious, that the transformations in chains either $1 \rightarrow 3 \rightarrow 2 \rightarrow 1$ or $4 \rightarrow 5 \rightarrow 6 \rightarrow 4$ proceed significantly faster than the transformations $3 \rightarrow 4$ or $6 \rightarrow 7$. In case studying the system with a certain equipment characterized by a reaction time comparable to the times characteristic of the more slow processes, details of the faster processes can not be observed. As regards the faster processes, only the mean values can be obtained this way, at the same time, the slower processes can be followed in details. Now, in a mobility spectrometer, in the course of measurement process ions drift from one electrode to another, whereas the drift time is at least some milliseconds. Consequently, in case of certain processes proceeding faster than some milliseconds, details of the processes can not be studied by mobility

spectrometry, as relative to mobility spectrometer that processes can be considered to be in equilibrium, therefore, only the equilibrium values (or mean values) can be measured.

Applying the consideration described above to the case depicted in Figure 2.2, the individual mobilities of ions 1–6 can not be obtained by mobility spectrometry, because within the process of measurement the nature of an individual ion, accordingly, also the actual mobilities of the ions are changed for many times due to fast reactions between the ions, owing to this, only a mean value can be observed. Therefore, in the case under discussion, three peaks are observed in the mobility spectrum: the first, corresponding to the mean mobility of ions 1–3, the second, corresponding to mean mobility of ions 4–6, and the third, corresponding to the actual mobility of ion 7

Thus, peaks of a mobility spectrum can not generally be considered to be determined by individual ions but, in general case, a certain peak is conditioned by a certain chain of reactions being in the state of equilibrium, at which height of the peak is determined by the summary concentrations of the ions belonging to the chain, and location of the peak is determined by mean mobility of the ions. The consideration can be illustrated as follows. In the paper (Mohnen, 1977) the system (X% $\text{H}_3\text{O}^+(\text{H}_2\text{O})_2$; Y% $\text{H}_3\text{O}^+(\text{H}_2\text{O})_3$, Z% $\text{H}_3\text{O}^+(\text{H}_2\text{O})_4$) has been studied by means of mobility spectrometry: that system became apparent in the shape of a single peak. In case the equilibrium of the system (X; Y; Z) was changed, e.g. because of a change in the concentration of water, it resulted in a change of the location of the peak. In case a new chain was added into the system, e.g. because the transformations $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k \rightarrow \text{NH}_4^+(\text{H}_2\text{O})_k$ became essential, it resulted in the additional peak.

The possible transformations of mobilities of the individual ions within a measurement process can cause an additional broadening of the peaks of mobility spectrum.

2.4.2. Some specific merits of the results obtained by mobility spectrometry

Because of the specific character of the conditions of measurements, the results obtained by mobility spectrometry are quite different from the results obtained by mass-spectrometry. By means of mass-spectrometry, mainly steady-state composition of ions and composition of very young ions have been studied. In return, by means of mobility spectrometry certain results have been obtained, characterizing the processes determining the composition of ions at the ages of ions being about 1 s. Besides, especially by mobility spectrometry the effects of the changes in the concentrations of several neutral gases on the composition of ions have been studied, at which certain gases having an essential effect on the composition of ions have been found out. Considering that, the fact that the known works dealt with simulation of evolution of ions (see survey in Article 2.2) have given very few attention to the results obtained by mobility spectrometry is a quite incomprehensible one. True enough, interpretation of the results obtained by mobility spectrometry is a little undefined, as described in Article 2.4.1, all the same, certain results can be used for improvement of the model. In the next articles we are going to deal with these results.

2.4.3. Effects of ion ageing and of air humidity on a mobility spectrum

One of the results obtainable by means of mobility spectrometry describes in general lines the transformations in the nature of ions conditioned by ageing of ions. To get the respective results, the spectrum of ions generated once at the initial moment is followed, at which the measurements are usually carried out in the ordinary laboratory air. The character of the transformations of spectrums obtained this way is commonly analogical to the ones depicted in Figure 2.1. As we can see, in case of ageing of ions the relative heights of several peaks change, that should mean a substitution of classes of ions, (see in Article 2.4.1), therefore, while the nature of ions changes, the age of ions can be estimated. Moreover, the ratio of masses of younger ions to masses of older ones can be estimated. The results depicted in Figure 2.1 correspond to the ages of ions being about 1 s. As it can be seen, in case of negative ions, the older ions should be lighter than the younger ones (Iher and Salm, 1981, Salm and Iher, 1983).

On ground of the results described last any stable conclusion about the nature of the ions can not be made, nevertheless, certain other conclusions can be. At first, a certain change in the nature of negative ions takes place just at the ages of ions from 0.2 s to 2 s, which fact is quite significant because, on the one hand, several works have given no attention to the transformations of so aged ions, and, on the other hand, the information makes the adjustment of certain characteristics of the model possible. Moreover, the fact that the younger negative ions are, at least ordinarily, heavier than the more aged ones deserves a certain attention as well because several known works have considered ions clustering more and more in course of their evolution. As regards positive ions (not depicted in Figure 2.1), the situation is somewhat different: in case of positive ions, it seems as if the analogical transformations take place at somewhat grander ages of ions because in the mobility spectrums of equal ages only the supposable outset of analogical processes is observable. As no mobility spectrum of more aged positive ions is known, the conclusion about analogical processes occurring also in case of positive ions is partially putative.

In the paper (Salm and Iher, 1983), dependence of mobility spectrum of ions on humidity has been studied as well. The results were analogical for ions of both signs, a sample of the results is depicted in Figure 2.1. As we can see, it seems as if an increased concentration of water slows down the processes leading to the terminal ions: in case of lower concentration of water the peak corresponding to the ions having larger mobilities is already formed, but in case of increased concentration of water, the same peak is still forming, and the peak corresponding to ions having smaller mobilities (which is dominant in case of younger ions) is still observable. Thus, evolution of negative ions at the ages near 1 s is quite sensitive to concentration of water: it seems as if the actual concentration of water determines the age when the class of younger ions is converted into the class of more aged ions. Besides, it seems as if the increased concentration of water makes the negative ions at the ages near 1 s somewhat heavier, which result was also confirmed for the ions at the ages of about a few milliseconds: in case of dry air the mean mobility was about $2.1 \text{ cm}^2/(\text{V}\cdot\text{s})$, at

13% of relative humidity, $1.58 \text{ cm}^2/(\text{V}\cdot\text{s})$ (Lawless and Sparks, 1980); the similar results were obtained by (Hayhurst *et al.*, 1992).

In case of positive ions, the results are preliminary and partially putative: according to the results obtained by (Salm and Iher, 1983), the processes can be guessed to be analogical to the ones of negative ions, only in this case, the transformations are to be considered to proceed more slowly. On the other hand, the results obtained by (Parts, 1988) have shown almost no dependence of evolution of positive ions at the ages near 1 s on the concentration of water, moreover, it seemed as if the increased concentration of water makes the positive ions lighter. The effect mentioned last was also observed by (Lawless and Sparks, 1980), in case ions at the ages of about a few milliseconds. Thus, any profound conclusion about the dependence of mobilities of positive ions on the concentration of water can not be made.

Mobility spectrum of ions at the ages between 0.2 s and 2 s has been observed also by (Nagato and Ogawa, 1988). The results obtained differ significantly from the results of other works: in case of negative ions, mobilities up to $5 \text{ cm}^2/(\text{V}\cdot\text{s})$ were observed, in case of positive ions, the upper limit was about $3 \text{ cm}^2/(\text{V}\cdot\text{s})$. The ions at the ages of about 1 s having mobilities to so large degree have not been observed in any other work. Besides, according to the paper (Nagato and Ogawa, 1988), mobilities of both positive and negative ions should decrease in the course of ageing, which result also does not accord with the results reviewed above.

The mobility spectrums of positive ions at the ages of 1 ms – 50 ms have been studied by (Takebe, 1974). At the age of ions being about 5 ms, the top of the spectrum was located at $1.45 \text{ cm}^2/(\text{V}\cdot\text{s})$, whereas at the age of about 50 ms, the top has moved to $1.2 \text{ cm}^2/(\text{V}\cdot\text{s})$. It is interesting, that in case of dry air the respective mobilities were not larger but lower, consequently, in case of dry air the ions were heavier. That result can be explained by means of the assumption, that the evolution of so young ions is already, at least partially, conditioned not by water but by other neutral gases, at which water hinders the other gases to take the effect. If so, behaviour of positive ions with respect to the concentration of water is indeed unlike the behaviour of negative ones: in case of negative ions, the increased concentration of water makes ions heavier. As known from Article 2.3.1, several neutral gases can indeed induce quite heavy positive ions, that was already by quite young ions, all the same that was observed only in case of anomalous high concentrations of the neutral gases. Therefore, the effect of positive ions becoming heavier, reviewed above, can be explained in two ways: first, assuming the results observed to be actually common: behaviour of positive ions with respect to the concentration of water is indeed unlike the behaviour of negative ones, that may be conditioned by a very active neutral gas having constantly quite large abundance, in accordance with the discussion presented in Article 2.3.2 that could be, e.g., some derivate of pyridine; secondly, the effects observed by (Takebe, 1974; Lawless and Sparks, 1980) may be due to the composition of neutral gases that was actually outside of control, therefore, containing a very large amount of some active species: in this case, the results are to be regarded as the particularly cases.

Thus, following the consideration started above, at the ages of ions being about 1 s, a change in the nature of ions should take place, at which the negative ions should become lighter. That result does not accord with known works reviewed in Article 2.2, e.g., the quite thoroughgoing papers (Kawamoto and Ogawa, 1984; Kawamoto and Ogawa, 1986) have compiled a model that results in ions becoming heavier in the course of ageing. Moreover, according to the models, at such ages all the transformations of ions should already be over, at the ages beyond 1 s only the steady state of ions should exist: all the reactions included in the models have an effect before 1 s.

As it has already been said in Article 2.2, the models (Kawamoto and Ogawa, 1984; Kawamoto and Ogawa, 1986) accord very well with the results of measurements of steady-state composition of ions. True, the papers have set only the study of steady-state composition of ions as the purpose, in this respect, the papers are excellent. Nevertheless, applying the models to the study of evolution of ions at the ages of about 1 s, the results will be inaccurate.

The age of ions being near 1 s is by many models and estimates regarded as a certain final limit beyond which no significant transformation of small ions takes place anymore, e.g., in the paper (Keese and Castleman, 1985) it was declared, that the terminal ions $H_3O^+(H_2O)_k(CH_3CN)_m$ should be formed within 1 s; the papers (Kawamoto and Ogawa, 1984; Kawamoto and Ogawa, 1986) were already mentioned above. On the contrary, results obtained by means of mobility spectrometry imply that this age is rather the limit of a next in order change of nature of ions, but not the final limit of transformations of small ions. Besides, the results obtained by mobility spectrometry imply, that the peculiarities of evolution of ions at the ages near 1 s, specially the ones of negative ions, are determined mainly by the actual concentration of water, at which an increased concentration of water hinders other neutral gases to take the effect. As regards positive ions, the dependence of the transformations on the concentration of water is more putative.

2.4.4. Dependence of mobility spectra on the concentrations of neutral gases. Negative ions

One of the first works considering variations in composition of air by means of mobility spectrometry is the paper (Tammet, 1975). It appeared, that the mobility spectrum of negative ions at the ages near 1 s is quite sensitive to the changes in the concentrations of several neutral gases. For instance, an addition of iodine in concentrations of about a few mikrograms per cubic metre led to remarkable transformations in spectrum, at which in case the concentrations were about a few hundreds mikrograms per cubic metre, any preliminary spectrum became transformed into spectrum, consisting of one certain peak only. As regards the ages of ions from 0.1 s until 2.5 s, the characteristic peak conditioned by iodine is independent also of the ages of ions. As the peak was quite characteristic and could be reproduced rather well, it was recommended for calibration of mobility spectrometer. The effects, analogical to the one of iodine could be obtained also by means of chlorine, bromine, and fluorine: all the gases led mobility spectrum of negative ions to certain characteristic peaks, the mobilities of the respective peaks were $1.75 \text{ cm}^2/(\text{V}\cdot\text{s})$, $1.92 \text{ cm}^2/(\text{V}\cdot\text{s})$, $1.54 \text{ cm}^2/(\text{V}\cdot\text{s})$, and $1.73 \text{ cm}^2/(\text{V}\cdot\text{s})$.

As to sensitivity, it was different in case of different gases, but in all mentioned cases nearly $1 \mu\text{g}/\text{m}^3$. The highest sensitivity was observed in case of chlorine: the characteristic features of the spectrum became evident at the concentration of about $0.1 \mu\text{g}/\text{m}^3$. Various but significant effects were observable also by several other neutral gases, one of the most peculiar effects became evident due to an addition of a mixture of sulfur oxides, that resulted in a large amount of heavier ions (see in Figure 2.3).

The results being of great interest have been obtained also by (Salm and Matisen, 1977). It was found out, that not only the gases mentioned above but also NO_2 , HCl , and HCOOH have all substantial effects on mobility spectrum of negative ions at the ages of about 1 s. Because of the gases enumerated, any spectrum of negative ions accumulates in one certain peak, at which mobility of the peak depends on the gas used. Unfortunately, the respective mobilities have not always been reported. Besides, nitric acid, ammonia, phenol, SO_2 , and freones F-12, F-22 and F-142 have been noted as well: these gases also had remarkable and characteristic effects on the shape of the spectrum, all the same, the effects were somewhat weaker, likewise, the effects were somewhat different: because of the gases mentioned last the spectrum did not accumulate in one peak. As to the gases enumerated in the first group, the concentrations leading to remarkable effects did not exceed $1 \text{mg}/\text{m}^3$; as to the gases enumerated in the second group, the necessary concentrations were sometimes considerably higher. Additionally, the list of gases, in case of addition any of them no effect could be observed was reported. These gases were such as: NO , CH_3OH , $\text{C}_2\text{H}_5\text{OH}$, H_2SO_4 , methane, acetaldehyde, acetic acid, CHCl_3 , CHBr_3 , methyl bromide, ethyl bromide, CCl_4 , propane, aniline.

The results reported by (Salm and Matisen, 1977) accord, in general lines, quite well with the results reviewed in Article 2.3.1. All the same, in case of $\text{C}_2\text{H}_5\text{OH}$, the results differ somewhat from the results reviewed in Article 2.3.1: according to the latter, ethanol should have a certain effect. On the one hand, the concentrations of ethanol reviewed in Article 2.3.1 were abnormally high, but, on the other hand, the reviewed ages of ions were much shorter than the ages used in the paper (Salm and Matisen, 1977), this should partially compensate the different conditions due to the abnormally high concentrations. As a conclusion, the problem conditioned by differences in case of ethanol remains unsolved. Besides, the result having showed no effect in case of H_2SO_4 also seems to be somewhat different from the results reviewed in Article 2.3.2: according to the latter, the air contains almost constantly a large number of ions including molecules of H_2SO_4 , owing to which an influence of H_2SO_4 could be assumed.

A specially comprehensive survey dealing with transformations of mobility spectrums conditioned by an increase in the concentrations of several neutral gases has been reported by (Iher and Salm 1982). In the paper, spectrums of ions of both signs at the ages of about 0.5 s have been observed. According to the character of the effects observed, the studied neutral gases were portioned out into three groups. As to the group including gases having showed the most remarkable effects, the features of the respective transformations were observable already at the concentrations of neutral gases being about $1 \mu\text{g}/\text{m}^3$.

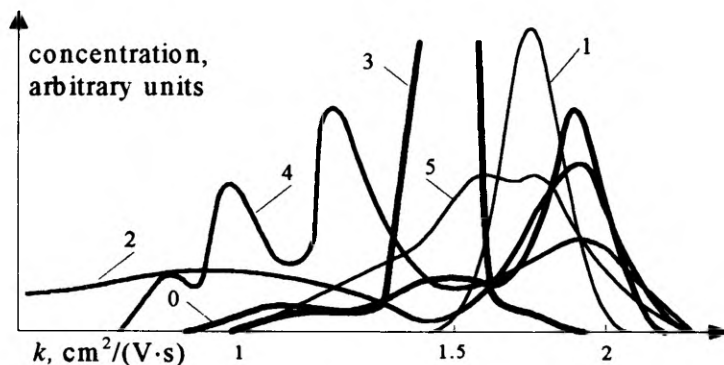


Figure 2.3. Variations of mobility spectrums of negative ions conditioned by an increase in the concentrations of certain neutral gases: 0– spectrum observed in the ordinary laboratory air, at ages of ions being about 2.5 s (Tammet, 1975); 1– spectrum conditioned by iodine (Tammet, 1975); 2– spectrum due to a mixture of sulfuric oxides (Tammet, 1975); 3– spectrum due to trichloroacetic acid (Iher and Salm, 1982); 4– spectrum due to $(C_4H_9)_2NH$ (Parts, 1992); 5– spectrum due to CH_3NH_2 (Parts, 1992).

In case of negative ions, the group which showed the most remarkable effects was as follows: water, ozone, H_2O_2 , benzene, chloroacetic acid, trichloroacetic acid, pyridine hydrochloride, nitric acid, F-22, chloroform, and all the gases mentioned above showed the most substantial effects. A very original effect was observed by trichloroacetic acid (see Figure 2.3): besides the transformations of the shape of the spectrum, likewise, the summary concentration of ions was increased. The effect mentioned last was not commented by (Iher and Salm, 1982). In other cases, the effects conditioned by the gases of this group were quite similar to one another: because of an increase in the concentration of a certain neutral gas, a certain peak of mobility spectrum became dominant, while other peaks became ordinarily smaller. NO_2 , HCl and HNO_3 all made the peak, located near $2.0 \text{ cm}^2/(V \cdot s)$, stronger, whereas, in case of chloroacetic acid, the respective peak was $1.75 \text{ cm}^2/(V \cdot s)$. Generally, the results reviewed here were close to the results reviewed above, all the same, nitric acid was above regarded as the gas having only a limited effect, and chloroform was above considered to have no effect.

The group of gases showing less substantial effects was as follows: acetone, formaldehyde, ethyl formiate, trichloroethylene, nitrobenzene, o-xylene, and ethanol. As to the differences, above in the paper (Salm and Matisen, 1977), ethanol was considered to have no effect. The list of the group of gases showing nearly no effect was the longest one: CO , CO_2 , H_2SO_4 , dibromoethane, dichloroethane, CH_3OH , diethyl ether, aniline, dimethyl formamide, methyl ethyl ketone, lactic acid, and many other gases. The list of the last group is quite similar to the analogical lists of other works.

The results reported by the paper (Iher and Salm 1982) make a good supplement to the results reviewed above. Nevertheless, certain questions remain

unanswered. In accordance with the discussion presented above, the influence of H_2SO_4 could be assumed, but no effect was actually observed. Moreover, the influence of CO_2 could be assumed because of the results reviewed in Articles 2.2 and 2.3.1: a change in the concentration of CO_2 should shift the equilibrium between ions $\text{CO}_4^-(\text{H}_2\text{O})_k$ and $\text{O}_2^-(\text{H}_2\text{O})_k$. On the other hand, the fact about the absence of any effect conditioned by a change in the concentration of CO_2 can perhaps be explained by the role of the age of ions: in case of the aged ions observed in the paper (Iher and Salm, 1982), both ions $\text{CO}_4^-(\text{H}_2\text{O})_k$ and $\text{O}_2^-(\text{H}_2\text{O})_k$ may already have been replaced by some other ions, as a result of which equilibrium between ions $\text{CO}_4^-(\text{H}_2\text{O})_k$ and $\text{O}_2^-(\text{H}_2\text{O})_k$ has no significance anymore. If so, we have got an additional result: in general case, at the ages of ions near 0.5 s, ions $\text{CO}_4^-(\text{H}_2\text{O})_k$ and/or $\text{O}_2^-(\text{H}_2\text{O})_k$ can not be met any longer.

In the paper (Nagato and Ogawa, 1988) it has been found out, that an increase in the concentration of HNO_3 results in heavier negative ions, which result is unlike the result reported by (Salm and Matisen, 1977): increased concentration of HNO_3 should result in a new peak having larger mobility.

In the paper (Hayhurst *et al.*, 1992), mobility spectrums of negative ions at the ages of about some milliseconds have been studied. The environment used included N_2 , O_2 , CO_2 , H_2O , O_3 , NO_2 , and a small amount of NO . The anomalous light ions reported do not accord with the ions obtained by other works. For instance, at the age of ions being about 10 ms ions O_2^- were found to be dominant. In conformity with the results reviewed in Article 2.2, the existance of such ions could be understandable in case of dry air, but not understandable in case characterized by the concentration of water equal to $2.7 \times 10^{15} \text{ cm}^{-3}$ as reported by (Hayhurst *et al.*, 1992): in this case, ions $\text{O}_2^-(\text{H}_2\text{O})_k$ should be present. Besides, the mobility of ions O_2^- should not be equal to $2.1 \text{ cm}^2/(\text{V}\cdot\text{s})$ as declared by (Hayhurst *et al.*, 1992), according with the results discussed in Article 1.2, the ions having such mobility should have masses of at least 55 a.m.u. In other respects, the mobilities of ions CO_4^- conditioned by CO_2 were found to be equal to the mobilities of O_2^- , which is also quite doubtful, and an increased concentration of water was found to make ions heavier, which accords with the results of several other works.

In the paper (Parts, 1992), the transformations of mobility spectrum of negative ions at the ages of about 1 s conditioned by methylamine, NNN'N'-tetramethylethyldiamine, tert-butylamine, dimethylamine, diethylamine, dibutylamine, and ammonia were studied. The concentrations used were $2.7 \times 10^{12} \text{ cm}^{-3} - 2.7 \times 10^{13} \text{ cm}^{-3}$. The studies resulted in some unprecedented shapes of spectrums, e.g., due to dibutylamine the spectrum including 4 peaks appeared (see Figure 2.3). The other amines had, in general, analogical effects: certain unprecedented peaks appeared, at which the respective mobilities were characteristic of individual amine. Certain differences were observed only in case of methylamine: a peak with a little lower mobility became evident (see Figure 2.3). The effect of ammonia was noticeable, but less substantial. The possible shapes of the reactions embracing amines were guessed as well.

As a summary, the following conclusions can be made. The shape of mobility spectrum of negative ions at the ages of about 1 s substantially depends on the concentrations of halogens, HCl , NO_2 , SO_2 , ozone, formic acid, certain freones,

chloroacetic acid, and amines (see also Figure 2.3), at which the concentrations necessary to cause remarkable transformations of the spectrum lie at about $1 \times 10^{12} \text{ cm}^{-3}$ – $1 \times 10^{13} \text{ cm}^{-3}$. The less substantial or disputable effects are conditioned by several gases, from which HNO_3 , H_2SO_4 , and $\text{C}_2\text{H}_5\text{OH}$ should be mentioned separately because the effects of the gases mentioned last regarded here as the less substantial ones should be out of any doubt if proceeding from results reviewed in Articles 2.3.1 and 2.3.2.

The shapes of the transformations of spectrum conditioned by an increase in the concentration of a certain gas are quite different: most of the gases having a substantial effect make a certain peak of the spectrum stronger, at the same time, other spectrum is often made weaker. Only the effects conditioned by amines are substantially different: in this case a spectrum with many peaks appears. In many cases the ions are transformed into the heavier ones, but in case of NO_2 it seems as if only the peak having the largest mobility by the present becomes dominant. In some cases it seems as if the ions becoming dominant were present (although in low concentrations) also in the natural spectrum, in other cases it seems as if the ions becoming apparent due to a change in the concentration of a certain gas are the absolutely new ones. Unfortunately, in several works the shapes of certain transformations have been left undefined.

2.4.5. Dependence of mobility spectra on the concentrations of neutral gases. Positive ions

In the paper (Kim *et al.*, 1978), spectrums of positive ions at the ages of about some tens of milliseconds have been studied. The environment was surely quite simple: mainly N_2 with a few additions, nevertheless, some interesting results have been obtained. According to the results, an increase in the concentration of NH_3 induced a certain peak which was found to be due to ions $\text{NH}_4^+(\text{H}_2\text{O})_n$, at the same time, the peak due to ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ disappeared. In case the peak due to ions $\text{NH}_4^+(\text{H}_2\text{O})_n$ were already present, an addition of ammonia had no effect: certain transformations of mobility spectrum were observable only in case a certain gas having proton affinity larger than NH_3 (e.g., pyridine or a certain amine) was added. The mobility of the peak due to $\text{NH}_4^+(\text{H}_2\text{O})_n$ was of $1.78 \text{ cm}^2/(\text{V}\cdot\text{s})$, methylamine induced the peak of $1.52 \text{ cm}^2/(\text{V}\cdot\text{s})$, ethylamine, the peak of $1.42 \text{ cm}^2/(\text{V}\cdot\text{s})$, because of pyridine, the peak of $1.27 \text{ cm}^2/(\text{V}\cdot\text{s})$ became apparent. The numerical values enumerated last have, above all, been intended for an illustration, as they do not have any self-dependent merit because the concentrations of the gases used have not been exactly defined in the paper (Kim *et al.*, 1978). The most important result of the paper (Kim *et al.*, 1978) consists in the list of neutral gases that can be characterized by the completely determined effects.

In conformity with the paper (Iher and Salm, 1982), transformations of mobility spectrum of positive ions were observable in case of trichloroethylene, dimethyl formamide, ethylene diamine, diethylene diamine, acetone, and dimethyl sulfoxide (see also Figure 2.4). The effects due to dimethyl formamide were analogical to the ones conditioned by dimethyl sulfoxide. The noticeable but less substantial effects were observed in case of $\text{C}_2\text{H}_5\text{OH}$, HCHO , and CH_3CHO . As regards the greater part of the gases studied, among these the gases not

mentioned here but mentioned in Article 2.3.4, no considerable effect was observed.

The results reviewed last in general lines accord quite well with the results reviewed in Articles 2.3.1 and 2.3.2. Nevertheless, the result which regarded ammonia as the gas having no effect is little incomprehensible: following the results discussed both in Articles 2.3.1–2.3.2 and by the paper (Kim *et al.*, 1978), the actual concentration of ammonia should be, at least in case of positive ions, quite substantial for the composition of ions. Maybe, the concentration of ammonia used in the paper (Iher and Salm, 1982) was actually close to the value leading the processes conditioned by ammonia to the state of saturation, in that case a further increase in the concentration had indeed no more effect.

In the paper (Parts, 1988), the transformations of mobility spectrums due to changes in the concentrations of several neutral gases have been studied in case of ions at the ages of about 1 s, the concentrations of neutral gases studied were about 10^{11} cm^{-3} .

According to the results obtained, also HCl should be quite essential to the composition of positive ions, namely due to an increase in the concentration of the new peaks located at $0.75 \text{ cm}^2/(\text{V}\cdot\text{s})$ and $1.25 \text{ cm}^2/(\text{V}\cdot\text{s})$ became dominant. The result is quite original: HCl has been studied also by (Iher and Salm 1982), but no effect on the spectrum of positive ions was observed. In case HCl is indeed essential to the composition of positive ions, it is one of the few gases having an influence both on negative and positive ions, at which in case of positive ions it leads to heavy ions. Nevertheless, so far no conclusion can be made.

Besides, a lot of gases have been studied in the paper (Parts, 1988): there was observed a strong influence of acetone, dimethyl sulfoxide, benzaldehyde ($\text{C}_6\text{H}_5\text{CHO}$), formamide, acetamide and dimethyl formamide (NH_2CHO , NH_2COCH_3 , $(\text{CH}_3)_2\text{NCHO}$), and similarly of benzonitrile ($\text{C}_6\text{H}_5\text{CN}$) and acetonitrile (CH_3CN), as less influential, ethyl ketone ($\text{CH}_3\text{COC}_2\text{H}_5$) and lactic acid ($\text{CH}_3\text{CHOHCOOH}$) were observed. The transformations of spectrum due to either acetone or dimethyl formamide were close to the ones conditioned by dimethyl sulfoxide, the transformations observed by benzaldehyde were close to the ones conditioned by collidine, the influence of acetonitrile was close to that of trichlorethylene (see Figure 2.4). Due to an increase in the concentration of acetonitrile, two isolated peaks of nearly equal heights located at $1.05 \text{ cm}^2/(\text{V}\cdot\text{s})$ and $1.3 \text{ cm}^2/(\text{V}\cdot\text{s})$ became apparent, due to formamide spectrum was converted into the shape of a very wide but nearly symmetrical peak top of which was located at $1.2 \text{ cm}^2/(\text{V}\cdot\text{s})$ and halfwidth of which was about $0.4 \text{ cm}^2/(\text{V}\cdot\text{s})$. Due to benzonitrile, the spectrum including a peak slightly stretched out in the direction of larger mobilities with a top at $1.05 \text{ cm}^2/(\text{V}\cdot\text{s})$ and with a halfwidth of about $0.4 \text{ cm}^2/(\text{V}\cdot\text{s})$ became apparent.

In the paper (Parts and Salm, 1992), substantial effects of pyridine and certain derivatives of pyridine on spectrum of positive ions became evident. The ions were about 1 s of ages, the concentrations of neutral gases added were surely below $1 \mu\text{g}/\text{m}^3$. The list of the gases studied was as follows: pyridine ($\text{C}_5\text{H}_5\text{N}$); 2-picoline ($\text{CH}_3\text{C}_5\text{H}_4\text{N}$); 2,4-lutidine and 2,6-lutidine ($(\text{CH}_3)_2\text{C}_5\text{H}_3\text{N}$); and γ -collidine ($(\text{CH}_3)_3\text{C}_5\text{H}_2\text{N}$). A sample of results is depicted in Figure 2.4.

As it can be seen from Figure 2.4, due to an increase in the concentration of pyridine, a new peak becomes dominant, whereas the peak can be either absolutely new or the old, already present in natural spectrum but very weak in case of natural spectrum. The effect of pyridine is quite similar to the one of dimethyl sulfoxide: due to both of the gases a peak with a larger mobility becomes stronger, while the peak with a smaller mobility becomes weaker. As to either dimethyl pyridine or trimethyl pyridine, an absolutely new peak becomes apparent, in other words, a new class of ions not existing under natural conditions comes into being. Let us now remind the results obtained by (Kim *et al.*, 1978): due to pyridine, the peak located at $1.27 \text{ cm}^2/(\text{V}\cdot\text{s})$ became dominant. Because of the undefined composition of the environment, the value does not have any self-dependent merit, all the same, it can be compared with the value obtained in the same paper in case of ions $\text{NH}_4^+(\text{H}_2\text{O})_n$: the mobility corresponding to the ions conditioned by pyridine was smaller. On the contrary, according to the paper (Parts and Salm, 1992), an addition of pyridine should result in ions having larger mobilities (see Figure 2.4). As regards the numerical values, they can not be compared with one another because in one case measurements were carried out in ordinary laboratory air, whereas in other case undefined composition of gases was used, moreover, the ages of ions were also different. Nevertheless, in one case the respective mobilities became larger, in other case smaller. That contradiction could be explained on the ground of assumption, that ions $\text{NH}_4^+(\text{H}_2\text{O})_n$ observed by (Parts and Salm, 1992) actually contained more water molecules than the analogical ions observed by (Kim *et al.*, 1978), yet, the assumption can not be proved in any way

In the paper (Parts, 1992), the transformations of mobility spectrum of positive ions at the ages of about 1 s conditioned by methylamine (CH_3NH_2), dimethylamine ($(\text{CH}_3)_2\text{NH}$), diethylamine ($(\text{C}_2\text{H}_5)_2\text{NH}$), tert-butylamine ($(\text{CH}_3)_3\text{CNH}_2$), dibutylamine ($(\text{C}_4\text{H}_9)_2\text{NH}$), NNN'N'-tetramethylethylenediamine ($(\text{CH}_3)_2\text{N}(\text{CH}_2)_2\text{N}(\text{CH}_3)_2$), and ammonia were studied. The concentrations used ranged from $2.7 \times 10^{12} \text{ cm}^{-3}$ to $2.7 \times 10^{13} \text{ cm}^{-3}$. It appeared, that the influence of amines on mobility spectrum is really significant (see Figure 2.4). The slightest transformations were observed in case of diethylamine, at the same time, due to dimethylamine the peak located at $1.2 \text{ cm}^2/(\text{V}\cdot\text{s})$ became weaker, and the peak of $1.4 \text{ cm}^2/(\text{V}\cdot\text{s})$ became stronger; due to dibutylamine the peak at $0.9 \text{ cm}^2/(\text{V}\cdot\text{s})$ became significantly stronger, as seen in Figure 2.4. Besides, due to methylamine ions became slightly lighter, as the peaks of natural spectrum became weaker, and a new peak with a somewhat increased mobility became apparent. The possible shapes of the reactions embracing amines were guessed as well.

As to ammonia, it was found to have a certain effect as well: the transformations conditioned by ammonia are depicted in Figure 2.4. Due to ammonia the dominant peak of natural mobility spectrum of positive ions becomes weaker, at the same time, the new peak with somewhat larger mobility becomes stronger, at which the new peak has a slightly larger mobility than the peak conditioned by methylamine. The result according to which ammonia should have a certain effect on mobility spectrum of positive ions seems to accord quite well with several other results: the ions containing ammonia have often been observed by means of mass-spectrometric measurements (see Article 2.3). All the

same, it should be mentioned that in several works ammonia has been regarded as a gas having nearly no effect, discussed hereinbefore.

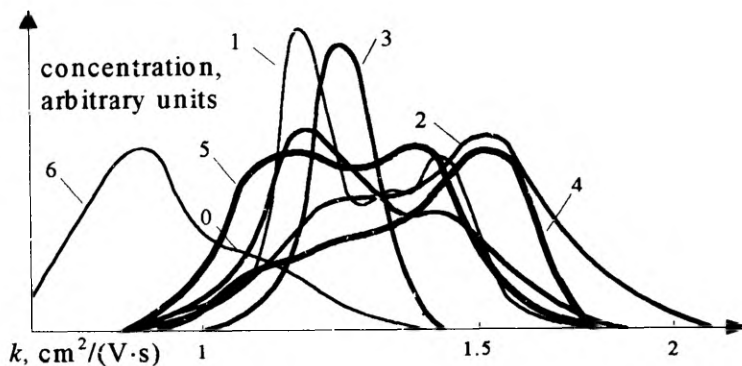


Figure 2.4. Variations in mobility spectrums of positive ions conditioned by an increase in the concentrations of certain neutral gases: 0– spectrum observed in case of ordinary laboratory air, the ages of ions being about 0.5 s (Iher and Salm, 1982); 1– spectrum due to trichlorethylene (Iher and Salm, 1982); 2– spectrum due to dimethyl sulfoxide (Iher and Salm, 1982); 3– spectrum due to collidine (Parts and Salm, 1992); 4– spectrum due to pyridine (Parts and Salm, 1992); 5– spectrum due to ammonia (Parts, 1992); 6– spectrum due to $(C_4H_9)_2NH$ (Parts, 1992).

As a summary, the following conclusions can be made. The shape of mobility spectrum of positive ions at the ages of about 1 s substantially depends on concentrations of acetone, trichlorethylene, dimethyl sulfoxide, benzaldehyde, acetonitrile, benzonitrile, pyridine, of several derivatives of pyridine, and of several amines (see also Figure 2.4). The effect of ethanol is less substantial. The additional concentrations inducing the remarkable transformations are lower than a few $\mu\text{g}/\text{m}^3$. Other effects observed are more problematical: in the paper (Parts, 1992) ammonia was found to have a remarkable effect, although the concentrations used were not defined, the results of other works reviewed have shown no remarkable effect. HCl was also found to have a certain effect, but this result was not confirmed by other works. The shapes of transformations observed were quite different: in case of ammonia an additional peak with a slightly increased mobility became apparent, due to trichlorethylene a spectrum including several peaks appeared, dimethyl sulfoxide and pyridine made the natural spectrum weaker and induced a new peak with a significantly increased mobility, a few gases, e.g. $(C_4H_9)_2NH$, induced a spectrum where very heavy ions should be met (see also Figure 2.4).

2.4.6. Altitude variation of the ion composition

In the previous articles we have dealt not only with the results obtained for near-ground air, but also with those obtained for higher altitudes, e.g., for stratosphere. Regarding that, an additional analysis of dependence of composition of ions on altitude is necessary.

According to the survey reported by (Meyerott *et al.*, 1980), the mean mobilities of positive ions are generally nearly inverse proportional to altitude: the factor of proportionality is about $1.0 \text{ cm}^2/(\text{V}\cdot\text{s})$ per 10 km (at the same time, a considerable number of results reported have significantly deviated from the relationship defined last). All the same, a relationship close to the one defined last has been reported also by (Sampath *et al.*, 1992), although only for altitudes of 50–70 km. Following the relationship, mobilities of the near-ground ions should be about $1.0 \text{ cm}^2/(\text{V}\cdot\text{s})$, which accords indeed many of results (see Article 2.4.7). Thus, in this respect the relationship may be valid. On the other hand, following the relationship, the near-ground ions should be different from: the ions observable at higher altitudes, e.g., in stratosphere: in accordance with Equation (1.2) with the reduction of mobilities done, at altitudes of about 20 km mean mass of ions should be almost 35 a.m.u., whereas the masses of near-ground ions should be about 10 times larger. If so, the results obtained for stratosphere have only a very limited value as to near-ground air.

Unfortunately, it seems as if the situation is not so clear: the results obtained for stratosphere (see survey in Articles 2.2 and 2.3) have shown ions much larger than 35 a.m.u., the ions observed were rather close to ions which could be guessed belonging to the near-ground ones (in accordance with Equation (1.2), the ions observed should have mobilities $k \approx 1.0 \text{ cm}^2/(\text{V}\cdot\text{s})$). The contradictions can be explained at least in three ways.

First, it is possible that heavier ions can actually be met quite frequently in stratosphere, as a consequence of which the relationship reported by (Meyerott *et al.*, 1980) can be regarded as a particular case only, but at the same time the results obtained for stratosphere should be quite applicable also to the near-ground air.

Secondly, it is possible that in the near-ground air layer, there are even heavier ions. In this case the results obtained for stratosphere were not applicable to the near-ground air. Nevertheless, it seems as if the second possibility is not very probable because the ions with mobilities significantly below $1.0 \text{ cm}^2/(\text{V}\cdot\text{s})$ are very unusual as to natural air (Tammert *et al.*, 1992), although they can become apparent due to increased concentrations of certain gases (Tammert, 1975; Parts, 1992; see also Figures 2.3 and 2.4), thus, at least the theoretical possibility of the existence of very heavy ions can not be excluded. As regards the real air, most likely only a few of the gases found to induce very large ions (see list in Articles 2.4.4, 2.4.5) are actually essential, namely, the gases have been contained also in the ions observed by mass-spectrometric measurements (see Article 2.3.2). As regards comparative measurements, in accordance with the review presented in Article 2.3.2, the negative ions similar to one another have been observed both in troposphere and stratosphere, although the portion belonging mainly to some undefined ions is more frequent at lower altitudes. In

case of positive ions the situation seems to be somewhat different, in this case the near-ground ions seem to be significantly more involved, it is likely because of a certain gases which can be met only in near-ground air, although the ions observed at higher altitudes are to be found as well. Thus, in case of positive ions at least the nature of a considerable portion of the ions seems to depend on the altitude.

Thirdly, let us assume the relationship reported by (Meyerott *et al.*, 1980) to be valid, and a significant portion of ions to be quite independent of altitude as if it seems to be at least in case of negative ions, as a result of this assumption, Equation (1.2) should not be valid in many cases. This result is imaginable (see discussion in Article 1.2), nevertheless, it can not be neither proved nor specified.

2.4.7. Mobility spectra of natural ions

In the papers (Tammet *et al.*, 1992; Salm *et al.*, 1992) a survey of long-time observations of natural mobility spectrums has been given. As to present work, two results are of particular interest.

First, ions with very low mobilities ($0.5 \text{ cm}^2/(\text{V}\cdot\text{s})$ and below) were observed, although the ions were very unusual. All the same, according to that the ions of such kind may indeed become apparent not only under artificial conditions (as reviewed in Articles 2.4.4 and 2.4.5), but also in the nature. As to the artificial conditions, such ions were observed in case of addition of a mixture of sulfuric oxides (see Article 2.4.4), also in case of increased concentrations of either HCl or $(\text{C}_4\text{H}_9)_2\text{NH}$ (see Article 2.4.5). As regards the paper (Tammet *et al.*, 1992), only quite unspecified assumptions of reasons leading to such ions were presented. Assuming the ions observed by (Tammet *et al.*, 1992) to be the same which were found out by the works reviewed in Articles 2.4.4 ja 2.4.5, under certain natural conditions the concentrations of the respective neutral gases should achieve quite high values. All the same, it is possible, that actually some other gases hereinbefore not considered to be responsible for very heavy natural ions, are still responsible, e.g. H_2SO_4 , molecules of which are contained in many negative ions (see Article 2.3). On the one hand, an addition of several molecules of H_2SO_4 to a negative ion may indeed cause the formation of a significantly heavy ion; on the other hand, H_2SO_4 was found to have no effect on the composition of ions at the ages near 1 s, as to the observations of mobility spectrums (see Article 2.4.4). As a result, the possible role of H_2SO_4 remains problematical.

Secondly, some results about dependence of mobilities of ions on temperature have been reported: in general lines, an increase in temperature induces a decrease of the mean mobility. The results observed were as follows: in case of positive ions, at temperatures of 0°C – 5°C the mean mobility was $1.48 \text{ cm}^2/(\text{V}\cdot\text{s})$, at temperatures of 10°C – 15°C $1.33 \text{ cm}^2/(\text{V}\cdot\text{s})$, and at temperatures of 20°C – 25°C $1.24 \text{ cm}^2/(\text{V}\cdot\text{s})$; in case of negative ions, the respective mobilities were $1.63 \text{ cm}^2/(\text{V}\cdot\text{s})$, $1.49 \text{ cm}^2/(\text{V}\cdot\text{s})$ and $1.41 \text{ cm}^2/(\text{V}\cdot\text{s})$. All the same, unlike the results reviewed the mobilities below $1 \text{ cm}^2/(\text{V}\cdot\text{s})$ have been reported by (Misaki, 1961). Nevertheless, dealing with the natural air usually the values near to the first ones are preferred (Mohnen, 1977). At the same time, the special cases characterized

by considerably lower mobilities can sometimes be present as well, as mentioned in the previous paragraph.

As to the reasons inducing the very heavy ions, some unknown neutral gases emission rates of which depend significantly on temperature were proposed by (Tammet *et al.*, 1992; Salm *et al.*, 1992). In principle, similar effects may be caused also by water because, on the one hand, the concentration of water vapour increases essentially if temperature increases; and, on the other hand, the results reviewed in Article 2.4.3 have shown a decrease in the mobilities of ions at the ages of about 1 s conditioned by the increased concentration of water. Moreover, some very heavy water clusters, e.g. $\text{H}_3\text{O}^+(\text{H}_2\text{O})_{20}$, have been proposed by (Parts, 1988) and by (Khan, 1994), as discussed in Article 2.2. However, usually the nature of natural ions is considered to be somewhat different, not based on large clusters of water (see overview in Articles 2.2, 2.3), owing to which, water could not be responsible for the heavy ions becoming sometimes apparent.

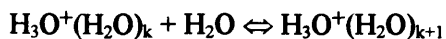
2.5. Factors of mutual transformations of ions

Up to now in this chapter we have dealt with the analysis of known data from the aspects of the factors having an effect on composition of ions. Now, we will make an attempt to compile a model describing the reviewed effects and dependencies as well as possible. Thus, matrix **A** of Equation (1.10) is to be determined, in other words, the ion-molecule reactions proceeding in the system are to be specified. As regards the concentrations of the neutral gases contained in the reactions, the concentrations of the gases are specified in the next Chapter, here we deal both with the choice of necessary reactions and with the specification of rate constants of the reactions.

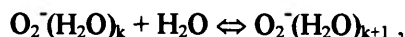
2.5.1. Principles of the selection of ion-molecule reactions

As said in Article 2.2, evolution of young ions can rather well be simulated by means of models proposed by (Huertas and Fontan, 1975; Huertas *et al.*, 1978). The models do not take the possible effects of several trace gases reviewed in Article 2.3.1 into account, all the same, they are quite satisfactory as to the conditions that can be met in the real air. As regards several trace gases, their effects become surely essential in case of more aged ions and can not be excluded from the model, still, the model of young ions can be taken as the basis for the improved model.

The model mentioned last mainly describes the formation of ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$ and $\text{O}_2^-(\text{H}_2\text{O})_k$. In general lines, the results obtainable are quite close to the ones obtained by means of measurements, nevertheless, any conclusion can not be made with respect to the accuracy of distribution of ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$ and $\text{O}_2^-(\text{H}_2\text{O})_k$ by k because the equilibrium constants, likewise the kinetic data of the reactions



and



were partially estimated in the papers (Huertas and Fontan, 1975; Huertas *et al.*, 1978) because of the absence of more accurate data. At the present time, some more data are available about the equilibrium constants (Keesee and Castleman, 1986), all the same, the data reported differ sometimes significantly from one another. Moreover, the actual internal distribution of water clusters of air is not well known. At the same time, the actual values of equilibrium constants are quite significant in respect to the behaviour of the model, as is discussed in Article 2.5.5.1. In the present work we make an attempt to adjust the model using both the known data about composition of young ions and data about more aged ions: it seems as if the effects conditioned by the actual values of the equilibrium constants become most evident in case of ions at the ages of about 1 s.

Next, the problem "which reactions should be included into the model" is to be solved. It is evident, that the many reactions will make the model more involved, at the same time, any essential reaction should be not excluded.

Every ion-molecule reaction is characterized by a certain rate constant. The values of rate constants can be very different, all the same, the collision value can not be exceeded. Under the conditions which can be met in the natural air, the collision value is about $1 \times 10^9 \text{ s}^{-1} \text{ cm}^{-3}$ that can be regarded as the upper limit of any rate constant.

In order a neutral gas could have an effect on steady-state composition of ions, the effect must appear at the latest at the age of about 10 s, but in case of dealing with younger ions, the effect must appear earlier. Consequently, the concentrations of the neutral gases of interest should have values above 10^6 cm^{-3} . Moreover, in common case any individual transformation proceeds more slowly as compared with the estimated upper limit. The upper limit can be the case only if the competing processes are absent, whereas by the presence of competing processes the transformation of interest can actually be quite slow, therefore, the concentrations of the neutral gases which may induce significant effects should be at least $10^7 \text{ cm}^{-3} - 10^8 \text{ cm}^{-3}$. As it is seen in Chapter 3, the concentrations of many gases do not exceed that value, at least as to the normal conditions. Therefore, limiting ourselves to the normal conditions only, those gases can be not included into the model. On the other hand, in some specific cases the concentration of a certain gas may significantly exceed the normal value, owing to which, those gases will not generally be excluded from the present model, but this is the case only if the other quantities describing the respective reaction are well known. Besides, by means of the procedure of separation of more essential variables described in Article 1.6, the reactions out of interest can be left aside any time. Nevertheless, any reaction should not be included into the model for the reasons mentioned hereinafter.

Consequently, the accurate concentrations of neutral gases have a great importance. Unfortunately, as seen in Chapter 3, the actual concentrations of many essential gases are not well known, and therefore, any model including such gases will be somewhat inaccurate regardless of other efforts. Therefore, other estimates should be avoided. In several known works also the rate constants have been estimated, e.g. the value $k = 1 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ can be met quite often. True, this way a good accordance with any result of measurement can be achieved quite easily, nevertheless, in the present work we are not going to take a

use of this. With respect to an individual reaction, we proceed from the requirement, that at least one, either the rate constant or the concentration of the neutral gas contained in the reaction must be accurate, otherwise the reaction will not be included into the model.

2.5.2. Preliminary model

A set of reactions can be compiled in two ways: first, one can take into account all the reactions available. secondly, one can proceed from the known behaviour and dependencies, further considering only the reactions describing the necessary effects. The first way results in a too voluminous model, the second results in the model where some essential but not obvious reactions may be left out. Following the second way, it is quite complicated to accomplish that all the necessary reactions were present in the model because of the involved character of the transformations of ions. In the present work we make an attempt to use a combined way: first, we will include most of the reactions met in two comprehensive tables, henceforth, we search and add the reactions which seem to be responsible for the known effects reviewed above. The first stage should result in a quite universal model with most of the essential processes taken into account already. Then, the second stage could be regarded as an adjustment of the model.

According to the discussion presented above, the evolution of young ions can be simulated quite satisfactory by means of models (Huertas and Fontan, 1975; Huertas *et al.*, 1978). Taking that into consideration, we have proceeded from these models. Henceforth, most of the reactions reported in the comprehensive table (Virin *et al.*, 1979) have been added, and after that most of the reactions reported by (Albritton, 1978) have been added as well. Unfortunately, oftentimes the same reactions were specified differently. In such cases the values of rate constants reported by (Huertas and Fontan, 1975; Huertas *et al.*, 1978) were replaced by the values reported by (Virin *et al.*, 1979), thereupon, the values obtained were replaced by the values reported by (Albritton, 1978) if needed.

In the course of the compilation of the model, the following reactions have been omitted: the reactions, studied at temperatures far from the normal ones, also the reactions, containing a neutral gas most likely not present as to the natural air (e.g., Li, Ca, Mg, Fe, Xe, D₂), likewise, the reactions requiring an ion which obviously was not produced by the remainder part of the system. In general case, the reactions rate constants of which were specified by a certain estimated value only, likewise, some reactions including a neutral gas actual concentration of which was not known and, at the same time, no effect due to which was observed have been omitted as well. The criterion mentioned last was applied most inconsistently: mainly the reactions containing a certain more complicated organic gas and producing only a new unknown terminal ion further not participating in any known process have been left out because the addition of such reaction would result in an additional variable of the system, which obviously would not be very substantial, either.

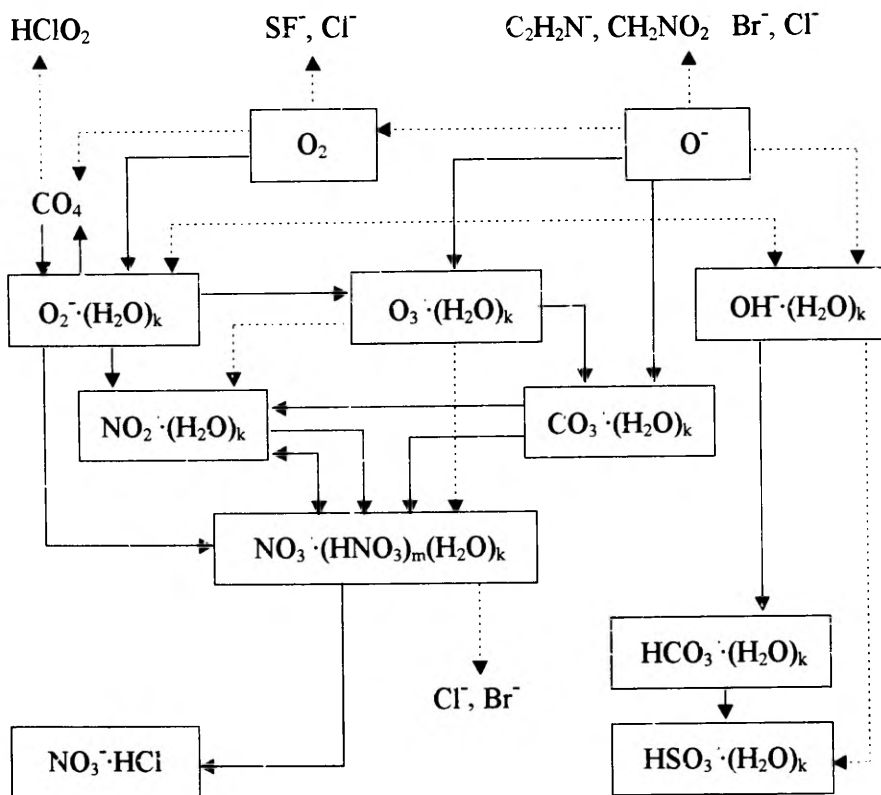


Figure 2.5. The scheme for most important transformations in the preliminary model of negative ions. The names surrounded by rectangles denote more important ions, the names without rectangles denote less important ions, the arrows denote reactions (continuous lines: more important reactions, dashed lines: less important reactions).

In this way the “preliminary model” has been obtained. Henceforth, the model was improved and adjusted in the manner which is described in Article 2.5.5.

Besides, the preliminary model has been analysed by means of the procedure described in Article 1.6. Following this line it was possible to isolate the most important processes of transformations, depicted in Figures 2.5 and 2.6.

By the use of Figures 2.5 and 2.6, the behaviour of preliminary model can be compared with the behaviour expected on the ground of the results reviewed above. We can see, that ions $\text{NO}_3^-(\text{H}_2\text{O})_k(\text{HNO}_3)_m$, $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$, and $\text{NH}_4^+(\text{NH}_3)_m(\text{H}_2\text{O})_k$ should be essential in accordance with both the preliminary model and the reviewed results: therefore, the preliminary model can, at least in principle, describe the evolution of the ions mentioned last. All the same, several effects obtained by virtue of measurements can not be described by means of the preliminary model: let us mention the ions including pyridine, likewise, the ions containing amines, also ions $\text{HSO}_4 \cdot \text{X} \cdot \text{Y}$. Consequently, the preliminary model is

to be improved. At the same time, by the use of Figures 2.5 and 2.6 the further improvement is more simple because both the main features of the model and the results of proposed changes can be followed quite easily.

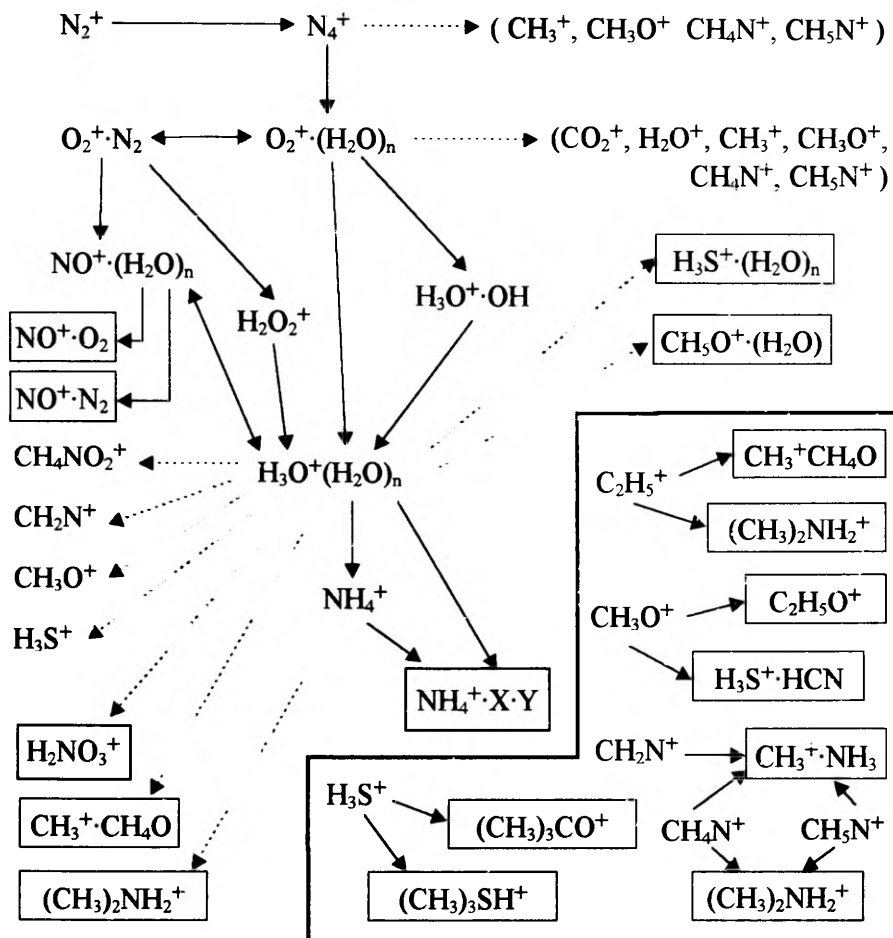


Figure 2.6. The scheme for most important transformations in the preliminary model of positive ions. The names surrounded by rectangles denote terminal ions, the names without rectangles denote transitional ions, the arrows denote reactions (continuous lines: more important reactions, dashed lines: less important reactions).

As it can be seen in Figures 2.5 and 2.6, certain ions have special qualities, namely most of the terminal ions are formed via the certain ions, which can therefore be regarded as the buffers of evolution of ions. In the first place, ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$, $\text{CO}_3^-(\text{H}_2\text{O})_k$ and $\text{O}_2^-(\text{H}_2\text{O})_k$ can be considered buffer ions. In common case, the buffer ions are formed at the ages below a few milliseconds, henceforth concentrations of the ions remain nearly constant up to the ages at which the processes of formation of the ions of the next stage (in certain cases:

terminal ions) become essential (see also Article 2.2). Commonly, formation of terminal ions does not start before some hundreds of milliseconds. At the same time, the rates of formation of the ions of the next stage depend significantly on the internal equilibrium of the buffer ions: the rates of the reactions proceeding from the buffer ions, e.g. from ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$, depend, in general case, on the individual value of k (Albritton, 1978; Viggiano *et al.*, 1982; Keesee and Castleman, 1985; Viggiano *et al.*, 1988a). As a rule, the reactions leading to the ions of the next stage proceed faster in case the respective initial buffer ions are lighter. Consequently, in case the equilibrium of buffer ions is shifted towards larger ions formation of terminal ions proceeds more slowly. According to the results of preliminary simulations, the effects conditioned by shifts in the equilibrium of buffer ions become apparent most of all in case of composition of ions at the ages of about 1 s. This was also the reason for a detailed consideration of the results obtained for ions at the ages of about 1 s, as done above.

Consequently, in the course of improvement of the model, the problem of adjustment of the equilibriums of the buffer ions is to be considered first of all. As to earlier works, the problem has oftentimes been considered a marginal one (Kawamoto and Ogawa, 1984; Kawamoto and Ogawa, 1986; Beig *et al.*, 1993a; Beig *et al.*, 1993b). Besides, the adjustment is quite complicated because the actual shapes of the equilibrium of buffer ions are not known, only the data about transformations of the nature of ions conditioned by their ageing (see review in Article 2.4.3) are available.

Moreover, both the rate and equilibrium constants required are insufficiently known: first, only the data covering the clusters with a small number of water molecules were reported, secondly, the data reported in different works have sometimes not accorded with one another (Keesee and Castleman, 1986). As was reviewed in Article 2.2, certain very heavy clusters should be specially stable. Unfortunately, these clusters can not be included into the model because of the absence of thermodynamic data.

In addition, the values of the quantities determining the state of equilibrium also depend both on temperature and pressure. Therefore, next, these dependencies will be under discussion.

2.5.3. Temperature dependence of the rates of ion-molecule reactions

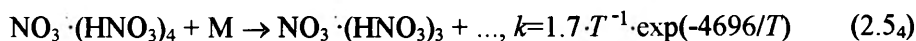
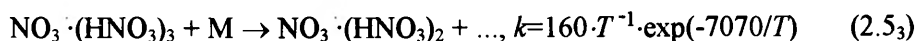
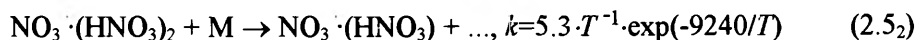
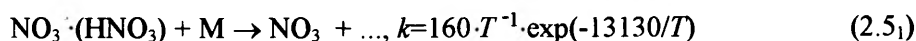
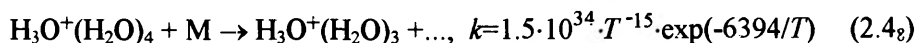
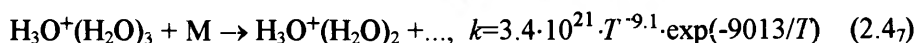
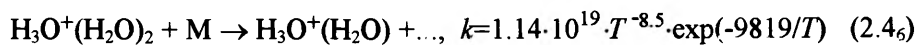
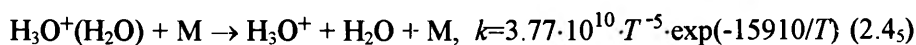
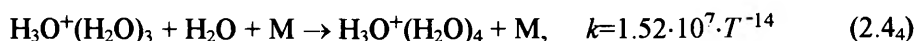
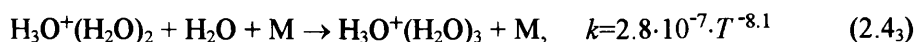
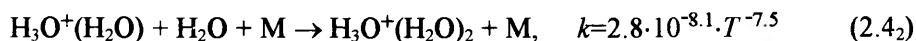
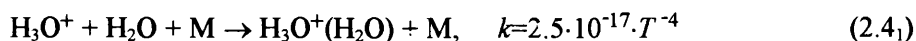
Commonly, Arrhenius equation describing the nexus between the value of a rate constant k and temperature T is known:

$$\ln k = \ln A - E/RT, \quad (2.2)$$

According to the equation, an increase in temperature causes an increase of rate constant, at which the latter increase may be quite substantial (Atkins, 1986). For instance, if activation energy E is about 0.1 eV, an increase in temperature from 243 K up to 303 K results in a nearly 3-times increase of rate constant, in case of higher activation energy the increase of rate constants is much larger. In general case, equilibrium constants depend on temperature as well:

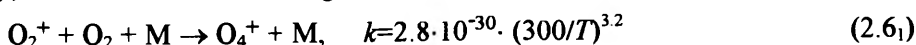
$$\left(\frac{\partial \ln K_p}{\partial T} \right) = \frac{\Delta H}{RT^2} \quad (2.3)$$

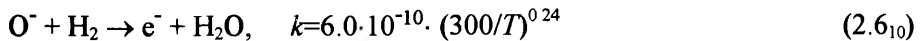
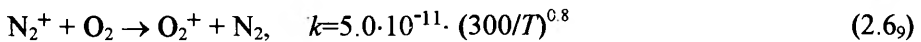
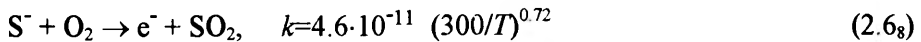
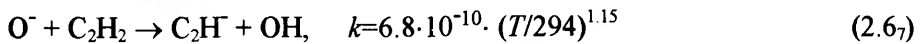
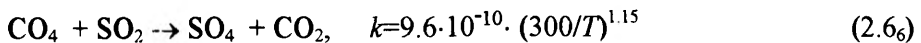
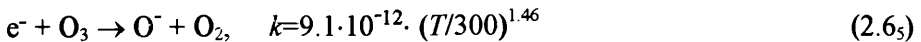
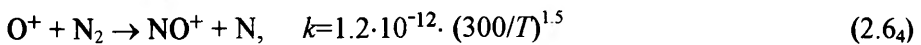
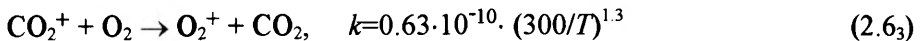
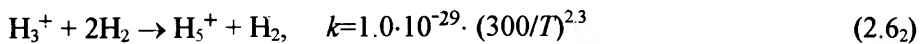
Thus, in principle the variations of both rate constants and equilibrium constants conditioned by a change in temperature may be quite essential, particularly in case the constants are obtained at temperatures far from the one of interest. All the same, the real situation is somewhat different. First, the results obtained at temperatures far from the normal one can be omitted because of the many results obtained at temperatures close to normal. Nevertheless, air temperature varies at least in a range between 243 K and 303 K, which may be sufficient to induce substantial variations in rate constants. Therefore, the problem of extents of actual changes of rate constant is to be discussed because Arrhenius equation is surely valid for many but not for any reaction: generally, the shape of dependence of a rate constant on temperature is quite individual. Let us look at some reactions:



Reactions (2.4₁) – (2.4₈) and (2.5₁) – (2.5₄) were reported by (Brasseur and Chatel, 1983). All the reactions enumerated last are significantly dependent on temperature, e.g., an increase in temperature from 243 K up to 303 K induces the following changes in the rate constants: in cases of reactions (2.4₄) and (2.4₈) about 20 times and 7 times, respectively, whereas the respective equilibrium constant changes about 140 times, at the same time the rate constant of the reaction (2.5₁) changes about 35000 times. Thus, reactions may be quite dependent on temperature not only theoretically but also in reality.

Nevertheless, not all the reactions of interest are so dependent on temperature, e.g., let us look at the following reactions:





Reaction (2.6₁) was reported by (Brasseur and Chatel, 1983), reaction (2.6₂) by (Hiraoka and Kebarle, 1975), reaction (2.6₃) by (Miller *et al.*, 1984), reaction (2.6₄) by (Dunkin *et al.*, 1968), reaction (2.6₅) by (Kawamoto and Ogawa, 1986), reaction (2.6₆) by (Viggiano *et al.*, 1989), reactions (2.6₇) and (2.6₈) by (Viggiano and Paulson, 1983), reaction (2.6₉) by (McFarland *et al.*, 1973b), reaction (2.6₁₀) by (McFarland *et al.*, 1973c). In case temperature increases from 243 K up to 303 K, rate constant of reaction (2.6₁) changes less than 2 times, rate constants of reactions (2.6₂) – (2.6₁₀) change even less.

As seen from the presented examples, not only the shape of the dependence but also the extent of the dependence are both quite individual. Generally, dependence on temperature is more substantial in case of clustering reactions, specially in case a large molecule is participating: the lower the binding energy of the complex formed, the stronger the dependence on temperature is (Bates, 1989). As to the reactions where not clustering but some other processes take place, then such reactions are generally quite independent of temperature, as also seen from the presented examples.

A certain rule, approximately common, can be set solely for the reactions including linear reactants without exceptions, in this case the shape of the rule is as follows:

$$k = k_0 \cdot (300/T)^n, \quad (2.7)$$

where the value of n is considered nearly 2; the case $n = 2$ is the reaction (2.8):

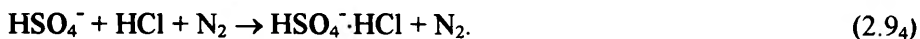


All the same, deviations from the mean value of n are quite frequent, e.g. in case of reactions (2.9₁) or (2.9₂):



where n is respectively equal to 3.2 or 4.4 (Bates, 1985a; Johnsen, 1986; Bates, 1989).

Generally, n may also depend on temperature and on the composition of the environment, e.g. in case of reactions (2.6₃), (2.9₃) and (2.9₄) (Lindinger *et al.*, 1975; Viggiano, 1986; Hiraoka, 1989).



In the paper (Meot-Ner and Field, 1978), an attempt has been made to set up correlations between the dependencies on temperature of the reactions that can be considered to be of second-order (reactions (1.3)) and certain other quantities of the reactions. Only organic compounds were studied. A certain correlation was found to be between n in Equation (2.7) and exothermity: the larger exothermity, the smaller n ; a weaker correlation was between the value of rate constant and that of n : the slower reaction, the larger n . Nevertheless, all the correlations found were too weak to set up any empirical formula. At the same time, it was found that n may be over 4 only in case of very solitary second-order reactions, at which all such reactions had rate constants below $k = 1 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$. Therefore, as to reactions (1.3), in case of a variation in temperature by 60 K, the induced change in the rate constant does not usually exceed 50%, in very rare cases the induced change can achieve 200–300%.

On the whole, it is clear that rates of reactions may depend on temperature, whereas in certain cases the dependence may be quite strong. On the other hand, no common rule can not be used to describe any dependence, that is specially essential because only the dependencies of a few reactions are actually known. As no common rule is valid, the dependencies of the reactions not studied in this respect can not actually be simulated in any way.

The fact, that regarding many reactions the actual dependence on temperature is not known, makes, no doubt, the model more inaccurate. On the other hand, that inaccuracy is not the only one. As already mentioned above, and likewise in several works, e.g. by (Brasseur and Chatel, 1983), any model of evolution of air ions is in practice determined by a considerable inaccuracy because of our limited knowledge. The situation is becoming better, nevertheless, several reactions of interest are not investigated as before, likewise, data about a certain reaction reported by different works differ up to several times from one another, likewise, much of data employed has been solely estimated. Moreover, the actual concentrations of many neutral gases are not exactly known (as shown in Chapter 3). Owing to the circumstances mentioned above, the model remains considerably inaccurate regardless of any effort to specify a certain or some certain values of the system, therefore, it seems as if it is not rational to make strong efforts in order to set up a few dependences on temperature. As already mentioned, nowadays only an estimate can be set as the purpose.

As a summary, it seems rational to distinguish between two cases. First, let us consider clustering reactions. As shown hereinbefore, in this case dependencies on temperature may be quite substantial: at an increased temperature equilibrium of cluster ions is shifted towards lighter ions. In this case the possible effects conditioned by variations in temperature should certainly be taken into account. This can be accomplished most easily by means of a few simulations for few

different temperatures, at which in case of absence of exact data the effects could be considered qualitatively, shifting equilibrium of the respective ions to some extent.

Secondly, as regards the reactions within which not clustering but some other processes take place, in this case the situation is somewhat different. As shown above, the dependencies of such reactions are considerably weaker, oftentimes not exceeding errors of rate constants themselves. Moreover, the actual dependencies of many reactions are not known. If so, it seems rational to omit all the dependencies on temperature except the single cases where the dependence is known to be large.

The decision not to take many effects due to temperature into consideration is supported by at least two facts of the case. First, as to earlier works having dealt with simulation of composition of ions, dependencies on temperature have generally been disregarded (Huertas and Fontan, 1975; Huertas *et al.*, 1978; Wisenberg and Kockarts, 1980; Beig *et al.*, 1993a; Beig *et al.*, 1993b); other works have confined themselves to the consideration about only a few known dependencies (Brasseur and Chatel, 1983; Kawamoto and Ogawa, 1986). Secondly, the measurement results about the actual variations in composition of ions conditioned by variations in temperature are practically absent, only the data reviewed in Article 2.4.7, according to which an increased temperature induces heavier ions, can be mentioned. Consequently, the results of simulation even obtained could not be justified because of lack of measurement data. Therefore, it seems as if it is not rational to give much attention to the study of effects conditioned by variations in temperature. The few results about effects due to temperature obtainable following the simplifications described above can be considered otherwise: in this way one can estimate the limits within which the composition of ions can vary.

2.5.4. Pressure dependence of the rates of ion-molecule reactions

The rate constant of an individual ion-molecule reaction does not depend on pressure because it characterizes the individual chemical transformation, surely, the shape of distribution of the equilibrium concentrations of the compounds contained in the reaction may depend on pressure, that is the case if the summary change in the number of moles of reactants is not equal to the summary change in the number of moles of reaction products. In such case the equilibrium constant of reaction K_p (independent of pressure) can be expressed in the shape (2.10):

$$K_p = (p/p_0)^{\Delta v} K_x, \quad (2.10)$$

where p_0 is the standard value of pressure (the value for which K_p has been tabulated); p is the actual pressure; Δv is the sum of all the stoichiometric coefficients of the reaction in which the coefficients belonging to the reactants are taken negative; and K_x is the product of molar concentrations of all the compounds contained in the reaction where the concentrations belonging to reactants appear in the denominator, the concentrations belonging to reaction products appear in the numerator (Knorre *et al.*, 1990; Atkins, 1986). Consequently, if $\Delta v = 0$ (e.g., in case of reaction (1.3)), K_x is likewise not dependent on pressure, but if $\Delta v = -1$, (e.g., in case of reaction (1.4)), the

steady-state concentrations of the compounds contained in the reaction depend on the pressure. Consequently, in case p is greater than p_0 , the rate of the direct reaction increases, which is equivalent either to a shift of the equilibrium towards reaction products, or to a relative increase in the abundance of reaction products. Besides, in this way the fact of an increased importance of the third-order reactions (1.4) at lower altitudes can be explained, while at higher altitudes only the second-order reactions (1.3) are significant. All the same, an increase in the rate of the direct reaction due to increased pressure does not mean an increase in the equilibrium constant: the increase in the rate is conditioned only by an increase in the pressure of reactants.

Thus, a change in pressure may result in a change in the list of essential reactions, therefore, having an effect also on evolution of ions. On the one hand, considering an individual reaction, no dependence on pressure can be observed: the individual reaction proceeds in same way both in stratosphere and in troposphere. On the other hand, near the ground some additional reactions which can not be noted at lower pressures because of their slowness may become substantial. The analogical situation can be observed while treating the available data about ion-molecule reactions: the data obtained at low pressures are surely valid as to near-ground layers, on the other hand, some important reactions may be left out of consideration if being limited to the data obtained at low pressures only.

The treatment used in the previous paragraphs is valid until the chemical process can be described by means of either Equation (1.3) or Equation (1.4) (Poltorak, 1991): in this case the pressure-dependence of reactions (1.4) can be described by means of Equations (2.10), (2.12₁), and (2.12₂), whereas reactions (1.3) are treated as the ones independent of pressure (Matsuoka and Nakamura, 1988). In case the chemical process can not be described either by means of Equation (1.3) or Equation (1.4) (that is most likely due to a complicated mechanism of the reaction), a change in pressure may result in a shift of equilibrium of intermediate phases of the reaction, that in their turn can result in a more complicated pressure-dependence of the whole reaction. As a matter of fact, the mechanisms of many reactions are quite complicated, owing to which the rate constants may still depend on pressure (Meisels *et al.*, 1978; Johnsen, 1986; Bates, 1989). As to theoretical works, different pressures are often considered differently (Viggiano, 1986). As to known data, most of the reactions (1.3) do not depend significantly on pressure, all the same, some reactions do, e.g. reactions (2.11₁) and (2.11₂) (Matsuoka and Nakamura, 1988), or reaction (2.11₃) (Hiraoka, 1989).



More detailed studies on dependencies of reactions (1.3) on pressure have been started only recently (Matsuoka and Nakamura, 1988). Nowadays only a little data about the actual dependencies is available. In principle, the problem is surely present: the main number of available data about constants of ion-molecule

reactions has been obtained at pressures of about 1 Torr (McFarland *et al.*, 1973a; Adams and Smith, 1976; Jennings, 1978; Keesee and Castleman, 1983, etc.), at the same time in certain cases the rate constants obtained at 1 Torr may differ at least 10 times from these but under atmospheric pressure (Smith *et al.*, 1989). Only by a few works the more high pressures have been used (Giles nad Grimsrud, 1992). Nevertheless, it is quite complicated to make a decision in which way the pressure should be introduced in the model because of the very limited data. The theoretical method of computation of dependencies on pressure introduced by (Smith *et al.*, 1989) is too involved to apply it for all the reactions of the system.

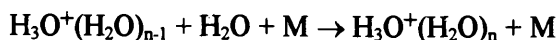
As regards earlier works concerning the simulation of evolution of ions, no special treatment of dependence on pressure has been applied: the constants of reactions have been considered equal to their tabulated values regardless of the pressure used in case of measurement of the constants. All the same, models are dependent on pressure, that is shown by following factors: first, concentration of the third body in reactions (1.4) depends on the pressure and is introduced by means of actual concentrations of neutral gases; secondly, in the works dealing with the lower altitudes a special attention is paid to the list of the third-order reactions; thirdly, a variation in pressure is taken into account at specification of equilibrium constants, according to Equations (2.12₁), (2.12₂).

In the present work we will follow the line used by earlier works as to dependencies on pressure.

2.5.5. Improvement of the preliminary model

2.5.5.1. Specification of the internal equilibriums of certain ion classes

Next, we are going to deal with improvement of the model described in Article 2.5.2. As said above, the problem of adjustment of equilibriums of the buffer ions is of the first-rate importance. First, let us consider the reactions determining the internal equilibrium of ions $H_3O^+(H_2O)_n$



The preliminary values taken from the paper (Huertas and Fontan, 1975) were mostly estimated. Now, the data reported by (Brasseur and Chatel, 1983) and (Lau *et al.*, 1982) are also available. As to the cases $n = 1..4$, the values of respective rate constants were reported, in cases of $n = 5..6$, only the thermodynamic data are available. Using the thermodynamic data, in the present work equilibrium constants K_c are computed by means of Equations (2.12₁) and (2.12₂) (Poltorak, 1991):

$$RT \cdot \ln K_a = -G_0 \quad (2.12_1)$$

$$K_c = K_a \cdot (c_0)^{\Delta v}, \quad (2.12_2)$$

where ΔG_0 is the change in Gibbs function due to the reaction, K_a is the dimensionless equilibrium constant expressed in terms of the chemical activities, K_c is the equilibrium constant of interest expressed in terms of the concentrations

(in units $\text{cm}^{-\Delta v}$), c_0 is the density of the environment under the pressure of interest (in units cm^{-3}), and the contents of Δv is the same as in Article 2.5.4. Near the ground, $c_0 = 2.7 \times 10^{19} \text{ cm}^{-3}$. In case we have reaction (1.3), K_c is dimensionless, in case of reaction (1.4), the dimension of K_c is cm^3 .

According to both the data reported by (Lau *et al.*, 1982) and the procedure described in the previous paragraph, two following reactions are specified:



and



The values of the equilibrium constants obtained in this way are the following: 1.5×10^{-15} and 1.5×10^{-16} (for 243K); 3.7×10^{-17} and 5.6×10^{-18} (for 303K), all in cm^3 . As the values of the respective rate constants are not known, we have proceeded from the fact, that the equilibrium of ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ is formed already at the ages below 1 ms (Lau *et al.*, 1982), therefore, the direct reactions can be considered quite fast, owing to which we have assumed all the rate constants of the direct reactions to be equal to $k = 1 \times 10^{-31} \text{ cm}^6 \text{ s}^{-1}$. As to the respective reverse reactions, their rate constants can now be calculated: $6.7 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$ and $6.7 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$ (for 243K); $2.7 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$ and $1.8 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$ (for 303K).

Besides, in the paper (Kochanski, 1985) formation energies of $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ obtained by means of calculations have been reported not only for $n = 5..6$ as by (Lau *et al.*, 1982), but also for $n = 1..9$. In conformity with the results, the differences between the formation energies of two consecutive clusters diminish quickly in case of small values of n , but in case of the values being over 5, the differences begin to diminish quite slowly, that is why, the ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ with n over 6 should be quite abundant, consequently, such clusters should deserve an attention. On the other hand, some results reported by (Kochanski, 1985) do not accord well either with the results obtained by (Lau *et al.*, 1982) or with the results of some other works, although the data about the same reaction but reported by different works are, as a rule, different as becomes clear from the survey (Keese and Castleman, 1986), therefore, the paper (Kochanski, 1985) is not exceptional in this respect. Nevertheless, as the data reported by (Kochanski, 1985) are the only one as to ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$, $n = 7..9$, we will confine ourselves to the ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$, $n = 1..6$.

All the same, certain results of (Kochanski, 1985) would be reviewed. According to the paper, and assuming the change in entropy ΔS_0 to be equal to that of the paper (Lau *et al.*, 1982), equilibrium constant of process



would be about $9 \times 10^{-20} \text{ cm}^3$ (at 300K) or about $1 \times 10^{-18} \text{ cm}^3$ (at 240K). Consequently, in case of the normal concentration of water, the equilibrium concentration of ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_9$ should be comparable to that of ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_8$, being only about 10 times lower than the latter. Therefore, assuming the results of (Kochanski, 1985) to be correct enough, ions with 9, and maybe with a larger number of water molecules should be taken into account

while considering ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$, but, on the other hand, the top of the shape of equilibrium distribution of ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ would be still located at $n = 3..5$ (at temperature 300K), or at $n = 5..7$ (at 240K); the ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ having larger values of n would in any case be less abundant.

Recently, some very large clusters like $\text{H}_3\text{O}^+(\text{H}_2\text{O})_{20}$ were proposed as well (Peifer *et al.*, 1989; Khan, 1994), but nowadays no thermodynamic data treating such clusters is available, therefore, no further consideration is possible.

As regards negative buffer ions, the data additional with respect to the preliminary model are practically absent. The thermodynamic data about reactions



and



reported by (Keese and Castleman, 1986) make the treatment possible up to ions $\text{O}_2^-(\text{H}_2\text{O})_4$ and $\text{CO}_3^-(\text{H}_2\text{O})_3$, at the same time the available kinetic data enable a treatment up to ions $\text{O}_2^-(\text{H}_2\text{O})_3$ and $\text{CO}_3^-(\text{H}_2\text{O})_2$ only (Albritton, 1978; Ikezoe *et al.*, 1987). Assuming the negative buffer ions being somewhat analogical to ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$, ions $\text{O}_2^-(\text{H}_2\text{O})_4$ and $\text{CO}_3^-(\text{H}_2\text{O})_3$ should not be the largest. As seen in case of positive ions, only the data about ions up to $\text{H}_3\text{O}^+(\text{H}_2\text{O})_6$ were available, at the same time it was likely that the ions with more great numbers of water molecules are actually present as well. The assumption about such analogy is supported also by the fact, that equilibrium constant of reaction



is about $9 \times 10^{-17} \text{ cm}^3$, and the constant of reaction



is about $2 \times 10^{-17} \text{ cm}^3$ (in accordance with Keese and Castleman, 1986), owing to which, the equilibrium concentrations of ions $\text{O}_2^-(\text{H}_2\text{O})_3$ and $\text{O}_2^-(\text{H}_2\text{O})_4$ are nearly equal, the same can be said about ions $\text{CO}_3^-(\text{H}_2\text{O})_2$ and $\text{CO}_3^-(\text{H}_2\text{O})_3$. Therefore, ions $\text{O}_2^-(\text{H}_2\text{O})_5$ and $\text{CO}_3^-(\text{H}_2\text{O})_4$ should be observable as well.

For that reason, in the present work we have proceeded from the data reported by (Huertas *et al.*, 1978) as to ions $\text{O}_2^-(\text{H}_2\text{O})_k$ and $\text{CO}_3^-(\text{H}_2\text{O})_k$ because this data is a most complete, describing also ions $\text{O}_2^-(\text{H}_2\text{O})_5$ and $\text{CO}_3^-(\text{H}_2\text{O})_4$, regardless of the matter, that the data were obtained partially by means of estimates. On the other hand, the data reported by (Huertas *et al.*, 1978) have been adjusted, namely the reported rate constants of reactions



and



have been diminished 5 times. It was due to two circumstances: first, in order to obtain the values closer to the ones reported by (Keese and Castleman, 1986),

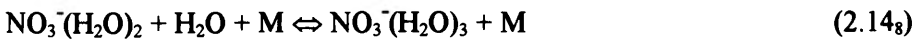
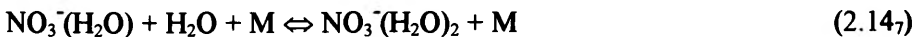
as to reaction (2.13₁); secondly, in order to achieve a better accordance with the known data treating the ageing of ions (see Article 2.4.3). As known from Article 2.4.3, at the age of about 0.5 s, nature of negative ions should change in some way, at which the actual age of the change should depend on the concentration of water. On the other hand, in case to follow the values reported by (Huertas *et al.*, 1978) as to reactions (2.13₁) and (2.13₂), nature of the ions is changed, but at the ages somewhat grander. In order to adjust the model in this respect, some reaction rate constants are to be adjusted, whereas this can be achieved most easily by means of the changes in the constants of reactions (2.13₁) and (2.13₂); moreover, that adjustment is supported also by the fact, that in this case the new rate constant of reaction (2.13₁) becomes closer to the one reported by (Keesee and Castleman, 1986).

As a result of the adjustment described above, the respective equilibrium constants acquire the values of about $2 \times 10^{-16} \text{ cm}^3$ and $3 \times 10^{-17} \text{ cm}^3$ (at 293K), or $7.5 \times 10^{-16} \text{ cm}^3$ and $7.5 \times 10^{-17} \text{ cm}^3$ (at 243K).

With certain reservations, ions $\text{NO}_3^- \cdot \text{X} \cdot \text{Y}$ can also be regarded as buffer ions: they are surely terminal ions in case of the preliminary model, but they are not with respect to the treatment presented in Article 2.5.5.2. As to the treatment, ions $\text{NO}_3^- \cdot \text{X} \cdot \text{Y}$ are in some respects analogical to ions $\text{O}_2^-(\text{H}_2\text{O})_k$ and $\text{CO}_3^{2-}(\text{H}_2\text{O})_k$. both of the ions can be regarded as the intermediate ones, at which the rate of formation of the ions of the next stage depends on the shape of internal equilibrium of intermediate ions. Therefore, the problem of adjustment of equilibriums of ions $\text{NO}_3^- \cdot \text{X} \cdot \text{Y}$ is of the first-rate importance as well.

All the same, the treatment can be applied only to cases where X and/or Y denote H_2O and/or HNO_3 molecules. In case ions $\text{NO}_3^- \cdot \text{X} \cdot \text{Y}$ contain some another molecules, the ions can not be regarded as the buffer ions anymore (see Article 2.5.5.2).

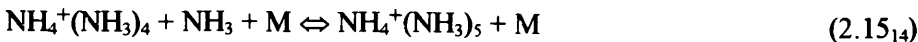
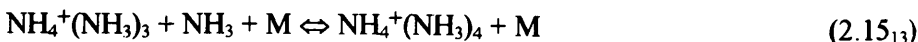
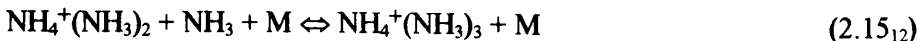
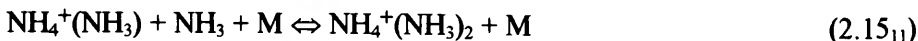
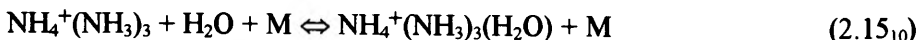
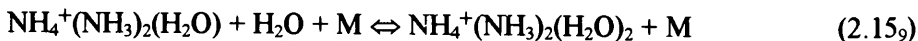
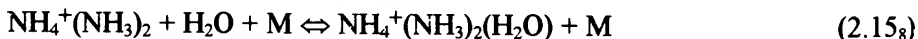
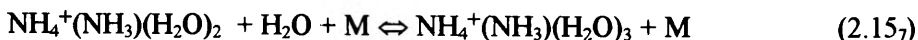
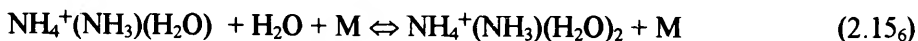
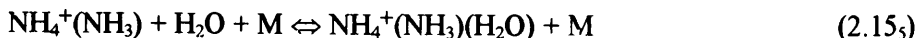
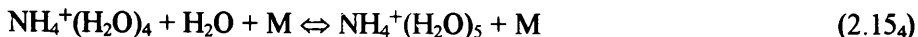
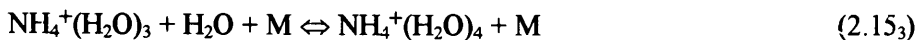
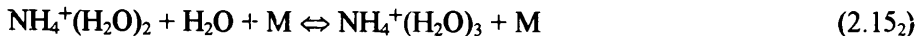
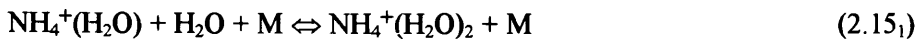
In the preliminary model only clusters $\text{NO}_3^-(\text{HNO}_3)_m \cdot (\text{H}_2\text{O})_n$ with m and n equal to 0, 1 or 2 were taken into account. Now, using the data reported by (Fehsenfeld *et al.*, 1975; Keesee and Castleman, 1986; Ikezoe *et al.*, 1987) the model can be supplemented: equilibrium constants of the following reactions can be specified:



The respective equilibrium constants become: $1.2 \times 10^{-6} \text{ cm}^3$, $3.7 \times 10^{-11} \text{ cm}^3$, $2.7 \times 10^{-14} \text{ cm}^3$, $5.2 \times 10^{-17} \text{ cm}^3$, $2.2 \times 10^{-18} \text{ cm}^3$, $9.4 \times 10^{-14} \text{ cm}^3$, $2.2 \times 10^{-15} \text{ cm}^3$, and $1.2 \times 10^{-16} \text{ cm}^3$ (at 243K); or $3.7 \times 10^{-9} \text{ cm}^3$, $6.2 \times 10^{-13} \text{ cm}^3$, $1.9 \times 10^{-15} \text{ cm}^3$, $9 \times 10^{-18} \text{ cm}^3$, $9 \times 10^{-19} \text{ cm}^3$, $5 \times 10^{-15} \text{ cm}^3$, $2.5 \times 10^{-16} \text{ cm}^3$, and $2.3 \times 10^{-17} \text{ cm}^3$ (at 303K). According to the kinetic data available, rate constant of the direct reaction of process (2.14₁) should be over $1 \times 10^{-26} \text{ cm}^6 \text{ s}^{-1}$. As no kinetic data is known about treating reactions (2.14₂) – (2.14₅), in the present work all direct reactions (2.14₁)–(2.14₅) are guessed to have the same rate constants equal to $1 \times 10^{-26} \text{ cm}^6 \text{ s}^{-1}$, after that rate constants of the respective reverse reactions acquire the values of $2.7 \times 10^{-18} \text{ cm}^3 \text{ s}^{-1}$, $1.6 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$, $5.2 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, $1.1 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$, and $1.1 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$ (at 303K). As to processes (2.14₆) – (2.14₈), only rate constant of the direct reaction (2.14₆) is known: $7.5 \times 10^{-29} \text{ cm}^6 \text{ s}^{-1}$. Because of shortage of the data, all direct reactions (2.14₆) – (2.14₈) are guessed to have the same rate constants, thus, rate constants of the respective reverse reactions obtain the values of $1.5 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$, $3 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$, and $3.3 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ (at 303K).

As to positive ions, ions $\text{NH}_4^+(\text{NH}_3)_m(\text{H}_2\text{O})_k$ are somewhat analogical to ions $\text{NO}_3 \cdot \text{X} \cdot \text{Y}$. Both of the ions are terminal ions as to the preliminary model, but they can not be considered terminal with respect to results presented in Article 2.5.5.3, at which rate of formation of the ions of the next stage depends on the shape of the internal equilibrium of ions $\text{NH}_4^+(\text{NH}_3)_m(\text{H}_2\text{O})_k$.

In order to supplement the preliminary model, the data reported by (Keese and Castleman, 1986) can be employed, by means of which the following reactions can be specified:



The respective equilibrium constants become: $4 \times 10^{-14} \text{ cm}^3$, $8 \times 10^{-16} \text{ cm}^3$, $3 \times 10^{-17} \text{ cm}^3$, $4 \times 10^{-18} \text{ cm}^3$, $4.4 \times 10^{-15} \text{ cm}^3$, $3 \times 10^{-16} \text{ cm}^3$, $2 \times 10^{-17} \text{ cm}^3$, $1.8 \times 10^{-16} \text{ cm}^3$, $1.4 \times 10^{-17} \text{ cm}^3$, $1.2 \times 10^{-17} \text{ cm}^3$, $1.5 \times 10^{-13} \text{ cm}^3$, $2 \times 10^{-15} \text{ cm}^3$, $2.3 \times 10^{-17} \text{ cm}^3$, and $8.5 \times 10^{-20} \text{ cm}^3$ (all for 298K).

Unfortunately, a very limited number of data treating of respective rate constants is known. As regards processes (2.15₁) – (2.15₄), only the rate constant of the reaction forming ions $\text{NH}_4^+(\text{H}_2\text{O})$ is available: $1 \times 10^{-29} \text{ cm}^6 \text{ s}^{-1}$ (Albritton, 1978). Since all the clustering reactions forming water clusters considered above were quite fast, in the present work all direct reactions (2.15₁) – (2.15₄) are guessed to have the same rate constants equal to $1 \times 10^{-29} \text{ cm}^6 \text{ s}^{-1}$. As regards processes (2.15₁₁) – (2.15₁₄), the direct reactions of processes (2.15₁₁) and (2.15₁₂) were found having rate constants of about $2 \times 10^{-27} \text{ cm}^6 \text{ s}^{-1}$ (Ikezoe *et al.*, 1987), the same value is guessed to characterize all direct reactions (2.15₁₁) – (2.15₁₄). As regards processes (2.15₅) – (2.15₁₀), no kinetic data belonging to analogical reactions is known, therefore, the processes can not be included into the model.

Proceeding from the guessed values mentioned above, rate constants of the respective reverse reactions become as follows: $2.5 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$, $1.2 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$, $3.3 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ and $2.5 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ ((2.15₁) – (2.15₄), 298K); $1.3 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$, $1 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, $9 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$, and $2.4 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$ ((2.15₁₁) – (2.15₁₄), 298K);

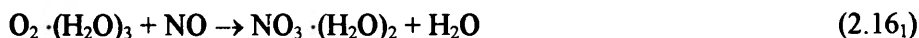
In this article we have dealt with adjustment of equilibriums of buffer ions. Next, the model would be adjusted with a respect to the effects described in Articles 2.2, 2.3.2, 2.4.4, and 2.4.5.

2.5.5.2. Improvement of the preliminary model: negative ions

As to negative ions, reactions (2.16₀)

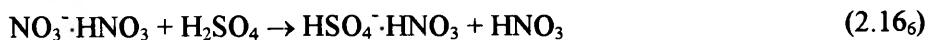


are substantial because the characteristics of these reactions determine not only the rates of formation of ions $\text{NO}_3^- \cdot \text{X} \cdot \text{Y}$, but also the rates of formations of the ions of the next stages. Certain additional data treating transformations (2.16₀) were reported by (Ikezoe *et al.*, 1987), true enough, in this work not ions $\text{NO}_3^-(\text{H}_2\text{O})_k$ but ions $\text{O}_2^- \cdot \text{NO} \cdot (\text{H}_2\text{O})_k$ were considered to be the reaction products. In the present work both of the ions are regarded as the same, after that it would be possible to specify two new reactions of interest:



with the rate constants of $1.5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ and $1.2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$

It is evident, that the preliminary model does not describe evolution of ions $\text{HSO}_4^- \cdot \text{X} \cdot \text{Y}$, which should be very essential as to observations (see Article 2.3.2). The data treating the respective reactions are available in the papers (Viggiano *et al.*, 1980; Viggiano *et al.*, 1982). According to the data, rate constants of reactions (2.16₃) – (2.16₇) are equal to $4.2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$, $2.7 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$, $2.6 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$, $2.3 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$, and ja $1.1 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$.



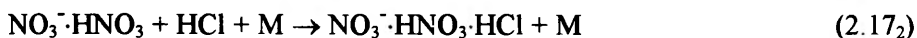
The rate constants of reactions (2.16₃) – (2.16₇) have all been obtained on the assumption that the rate of the fastest process in the system was equal to the collision rate. This assumption has been made because the actual concentration of H₂SO₄ could not be measured, as a result of which, a different base was inevitable (Viggiano *et al.*, 1980; Viggiano *et al.*, 1982). Therefore, in principle the rate constants of all reactions (2.16₃) – (2.16₇) may be overrated.

As regards the reactions reverse relative to (2.16₃) – (2.16₇), no data treating such reactions was found in (Albritton, 1978; Keesee and Castleman, 1986; Ikezoe *et al.*, 1987), owing to which reactions (2.16₃) – (2.16₇) should be practically one-directional. Since ions NO₃⁻·X·Y were at the same time the main terminal ions as to the preliminary model, introduction of reactions (2.16₅) – (2.16₇) is similar to that of new terminal ions HSO₄⁻·X·Y, while the actual part of ions HSO₄⁻·X·Y will now depend only on the actual rates of the reactions. In their turn, the rates depend on the actual concentration of H₂SO₄, therefore, the knowledge treating the concentrations of H₂SO₄ has the first-rate importance. Unfortunately, the concentrations of H₂SO₄ are actually not well known (see Chapter 3). Moreover, the rates of reactions (2.16₁) – (2.16₅) are not very sure as was shown above, as a result, the model is in effect quite inaccurate as to evolution of ions HSO₄⁻·X·Y. On that account, it seems as if it would not be rational to follow the treatment of internal structure of ions HSO₄⁻·X·Y that was developed by (Kawamoto and Ogawa, 1984; Kawamoto and Ogawa, 1986), at least as regards the ions where X and Y signify the molecules of H₂O, H₂SO₄ and/or HNO₃. It seems as if it would be rational to be limited to an “ion” HSO₄⁻·X·Y, which denotes all the ions of that class. On the substance, the new treatment does not make the model significantly worse because, on the one hand, ions HSO₄⁻·X·Y are terminal anyway, as to the known data. Consequently, there is no necessity to consider further transformations, and, on the other hand, the results obtainable by means of a model can be compared mainly with the data containing information only about the summary concentrations of certain classes of ions (see Articles 2.3.2, and 2.4.1 – 2.4.7), but nearly no information concerning the concentrations of individual ions. Therefore, the results treating the individual concentrations of ions HSO₄⁻·X·Y even if obtained, can not be justified because of shortage of measurement results.

The case in which certain ions having cores HSO₄ react with HCl molecules would be considered separately from “ions” HSO₄⁻·X·Y because it seems as if HCl has certain original qualities: it is almost the only gas capable of substituting the molecules of H₂O, H₂SO₄, and also HNO₃, as to ions HSO₄⁻·X·Y (Viggiano *et al.*, 1985; Ikezoe *et al.*, 1987), at the same time the molecules of HCl having taken a place either in ions HSO₄⁻·X·Y or in ions NO₃⁻·X·Y can not be relieved

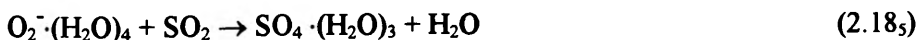
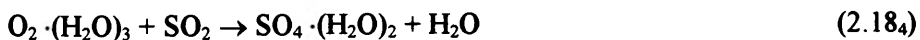
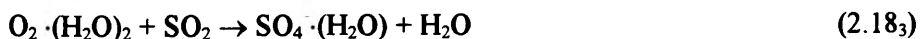
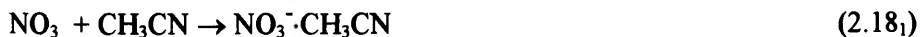
by any other molecule, as to the known data. Therefore, the ions including HCl molecules should be regarded as the apart terminal ions. As regards the results obtained by means of mass-spectrometric measurements, the ions including HCl molecules have only slightly been mentioned, all the same, mobility spectrums have been shown quite strong dependence on the actual concentration of HCl (see Article 2.4.4). On the other hand, the reactions including HCl, CFCI₃, CF₂Cl₂ or ClO molecules are found to be generally endergonic, and therefore, very slow (Fehsenfeld *et al.*, 1976). Moreover, no reaction resulting in other specific ions due to HCl is known, owing to which it seems as if the new peak observed in mobility spectrum due to HCl (see Article 2.4.4) was actually conditioned by ions NO₃·X·Y and/or HSO₄⁻·X·Y containing the molecules of HCl. Therefore, such ions should be considered separately.

Considering that, the following reactions have been added into the present model:



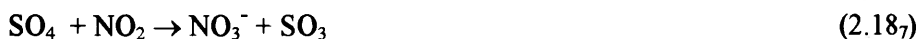
Rate constants k_0 of reactions (2.17₁) – (2.17₄) have the following values: $5 \times 10^{-28} \text{ cm}^6 \text{ s}^{-1}$, $2 \times 10^{-27} \text{ cm}^6 \text{ s}^{-1}$, $5 \times 10^{-28} \text{ cm}^6 \text{ s}^{-1}$, and $2.1 \times 10^{-27} \text{ cm}^6 \text{ s}^{-1}$. All the reactions are quite dependent on temperature: $k_1 = k_0(300/T)^{2.6}$; $k_2 = k_0(300/T)^4$; $k_3 = k_0(300/T)^{5.5}$, and $k_4 = k_0(300/T)^3$. It was said, that in principle the clusters with up to 4 molecules of HCl (e.g., HSO₄⁻·(HCl)₄) should be feasible, nevertheless, no data treating the respective reactions is known.

In Articles 2.3.2 and 2.4.4 several ions and neutral gases which should be substantial with respect to evolution of negative ions (C₃H₃O₄, CH₃SO₃, SO₂, CH₃NH₂, (C₄H₉)₂NH jt.) were pointed out. Unfortunately, the known data do not make simulation of all the effects possible. The preliminary model has been compiled on the ground of the data reported by (Albritton, 1978; Virin *et al.*, 1979): most of the data found in these works have been added into the model, as described in Article 2.5.2. Unfortunately, the comprehensive work (Ikezoe *et al.*, 1987) was received too late in order to take all these data into account, all the same the data describing the reactions proceeding from ions O₂⁻(H₂O)_k, CO₃⁻(H₂O)_k, or NO₃·X·Y have been considered. The reactions mentioned last were preferred because ions O₂⁻(H₂O)_k, CO₃⁻(H₂O)_k, and NO₃·X·Y should be specially important as described hereinbefore. Therefore, the following reactions of interest have been found out:

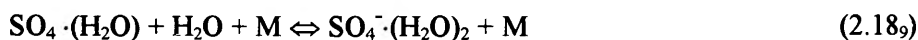


Reactions (2.18₁) – (2.18₅) should have the rate constants of $7.8 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, $1.8 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$, $1.7 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$, $1.7 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$, and $1.6 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$, respectively.

It seems as if reactions (2.18₂) – (2.18₅) imply that ions $\text{SO}_4 \cdot (\text{H}_2\text{O})_k$ constitute an additional class of terminal ions. Nevertheless, two reactions proceeding from ions $\text{SO}_4 \cdot (\text{H}_2\text{O})_k$ are known as well: reactions (2.18₆) and (2.18₇) with the rate constants of $2.5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ and $1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ respectively (Ferguson, 1973). On the other hand, it seems not plausible that reactions (2.18₆) and (2.18₇) were, as a matter of fact, the only reactions proceeding from ions $\text{SO}_4 \cdot (\text{H}_2\text{O})_k$ as at the same time a considerable number of reactions within which ions $\text{SO}_4 \cdot (\text{H}_2\text{O})_k$ are formed is known, therefore, a certain shortage of balance may be present as to reactions (2.18₂) – (2.18₇), as a result of this shortage an excessive amount of ions $\text{SO}_4 \cdot (\text{H}_2\text{O})_k$ may appear in the model.



Taking both the likely shortage mentioned above and the fact, that only equilibriums (2.18₈) and (2.18₉) can be specified on the ground of known data (Keesee and Castleman, 1986) into consideration, only reactions (2.18₁) – (2.18₄), and (2.18₆) – (2.18₉) can be added into the present model.



The equilibrium constants of processes (2.18₈) and (2.18₉) should have the values of $2.2 \times 10^{-16} \text{ cm}^3$, and $5.5 \times 10^{-19} \text{ cm}^3$, respectively (at 296K). As to kinetic data, none is available, owing to which in the present work a value of $1 \times 10^{-29} \text{ cm}^6 \text{ s}^{-1}$ has been guessed in case of the direct reactions because of several reactions consisting in clustering of water molecules onto an ion having nearly identical rate constants as shown above. In this case rate constants of the reverse reactions have values $4.5 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$, and $1.8 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$.

CH_3CN has been found quite substantial with respect to measured composition of ions as shown above, all the same, only reaction (2.18₁) is available. It is true, many respective reactions proceeding from ions $\text{OH} \cdot (\text{H}_2\text{O})_k$ are known (Hierl *et al.*, 1987), but these reactions should be of smaller importance in effect because the abundances of ions $\text{OH} \cdot (\text{H}_2\text{O})_k$ are actually very low as compared with the abundances of ions $\text{O}_2^- (\text{H}_2\text{O})_k$, $\text{CO}_3^- (\text{H}_2\text{O})_k$ and $\text{NO}_3^- \cdot \text{X} \cdot \text{Y}$.

As it can be pointed out from the discussion presented above, several effects reviewed in Articles 2.3.2 and 2.4.4 can not actually be simulated because of shortage of data. The results obtainable by means of the present model are reviewed in Chapter 4.

2.5.5.3. Improvement of the preliminary model: positive ions

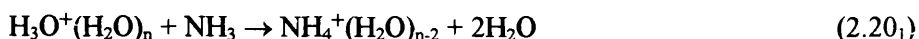
As said above, most of the data found in the works (Albritton, 1978; Virin *et al.*, 1979) have already been added into the model. Henceforth, we will deal only with the reactions proceeding from ions $\text{H}_3\text{O}^+ (\text{H}_2\text{O})_n$ or $\text{NH}_4^+ (\text{NH}_3)_m (\text{H}_2\text{O})_k$ because

these ions were found to be central in the evolution of positive ions (see Article 2.5.2).

With respect to positive ions a correct specification of processes (2.19)



is very important because these processes determine the rates of formation of all terminal ions. As to the processes, diverse data are available. In the work (Ikezoe *et al.*, 1987) only the data for the cases $n < 4$ were reported: the respective rate constants were about $2.2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ in case $n = 1, 2$, and about $1.8 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ in case $n = 3$. According to the paper (Ziereis and Arnold, 1986), rate constants of reactions (2.19) should be nearly independent of n (at least up to $n = 8$), all the rate constants should be about $1 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$. Most of the new data, as far as known, was reported by (Viggiano *et al.*, 1988a): reactions (2.19) were studied up to $n = 11$, all the same, only the data for cases $n = 2, 3, 4$ were reported in case of temperature being about 300 K, the respective rate constants were $1.9 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$. Besides, the most likely shape of processes (2.19) was thought to be (2.20₁):

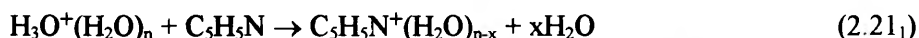


Reactions (2.20₂) were studied as well, in case $n+m < 5$ the respective rate constants were found to be about $1.9 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$



As to the present model, both reactions (2.20₁) and (2.20₂) have been included, being in accordance with the results reported by (Viggiano *et al.*, 1988a).

As reviewed in Articles 2.3 and 2.4.5, among positive ions, the ions containing pyridine are considered to be of great importance. In conformity with the papers (Viggiano *et al.*, 1988a; Viggiano *et al.*, 1988b), reactions (2.21₁) and (2.22₂) have been added to the present model:

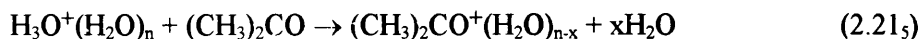
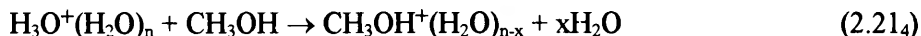
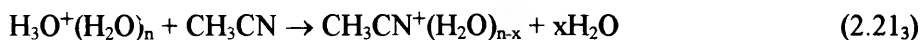


Reactions (2.21₁) can be specified in case of $n = 1, 2, 3, 4$: in case of $n = 4$ the respective rate constant $k_1 \approx 2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$, at which $k_1 \sim (300/T)^{0.9}$, in cases of smaller values of n the respective rate constants k_1 are about 10% larger. Rate constants of reactions (2.21₂) are $k_2 \approx 3.2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ (in case $n+m < 2$), or $k_2 \approx 1.9 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ (in case $n+m \approx 10$). As regards the distribution of the individual products of reactions (2.21₁) or (2.21₂), the individual parts are not known, as a result of which "ion" $\text{C}_5\text{H}_5\text{N}^+ \cdot \text{X} \cdot \text{Y}$ which denotes all the ions of that class, has been introduced. On the substance, such treatment does not make the model significantly worse as it was already explained in case of analogical treatment of ions $\text{HSO}_4^- \cdot \text{X} \cdot \text{Y}$ (see Article 2.5.5.2).

Several reactions including picoline were also reported by (Viggiano *et al.*, 1988b). Indeed, according to Article 2.4.5, the effect of picoline has been found to be significant. All the same, the actual concentrations of picoline are not known, and, moreover, the reactions are quite analogical to the ones including

pyridine, generating only a new class of terminal ions but no other changes as to the structure of the model, that is why the reactions including picoline have not been added into the present model.

The reactions including CH_3CN , CH_3OH or $(\text{CH}_3)_2\text{CO}$ available in (Viggiano *et al.*, 1988a) have been added into the present model as well:



These reactions are analogical to the ones including picoline, discussed above, but, on the other hand, the actual concentrations of CH_3CN , CH_3OH and $(\text{CH}_3)_2\text{CO}$ are better known. According to the data reported for the case of $n = 4$, the rate constants of reactions (2.21₃) – (2.21₅) should be $3.1 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$, $1.7 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$, and $2.0 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ respectively, whereas the values depend on n , decreasing about 10% in case of $\Delta n = +1$. Alike ions $\text{C}_5\text{H}_5\text{N}^+ \cdot \text{X} \cdot \text{Y}$ discussed above, the individual parts of products of reactions (2.21₃) – (2.21₅) are not known, and therefore, three new “ions” which denote the ions of that class altogether, have been introduced, that was the case also with ions $\text{C}_5\text{H}_5\text{N}^+ \cdot \text{X} \cdot \text{Y}$

Unfortunately, several effects reviewed in Article 2.4.5 can not be simulated because of absence of data concerning the respective reactions. On the other hand, the data treating the reactions containing $\text{C}_5\text{H}_5\text{N}$, CH_3CN , CH_3OH , or $(\text{CH}_3)_2\text{CO}$ show a similar nature of these reactions: all the reactions proceed via ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$, which consequently have a central role in the evolution of positive ions (see also Article 2.5.2). Therefore, it is quite likely that also most of the other transformations unknown yet, but possible to guess according to the effects reviewed in Article 2.4.5 proceed from ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$, owing to what in the future first of all such reactions should be searched.

3. CONCENTRATIONS OF NEUTRAL GASES

There are hundreds of gases participating in ion-molecule reactions proceeding in the troposphere. All models of ion evolution do not take all the gases into consideration, but in case we are dealing with the improvement of the model, we see, generally, more and more neutral gases becoming unavoidable. In the present model 150 different neutral gases are involved in the reactions. The neutral gases are enumerated in Table 3.2.

In order to describe neutral gases in a model one has to specify the values of concentrations of gases. This way one determines the matrix **A** in the equation of evolution of ions (1.10), according to the Equations (1.5) and (1.6). The problem of describing of neutral gases is not trivial for reason that the actual concentrations of several neutral gases important for simulating of troposphere are not exactly known. In this chapter we are going survey the current knowledge of the concentrations of the most essential neutral gases. Additionally, we are going specify the values of the concentrations, which are considered natural in the present work; the values are presented in Table 3.2. All the concentrations are given in cubic centimetres.

3.1. Main compounds of the air

Air molecule (usually used as the third body in ternary reactions (1.4)). The concentration of this component can be found out by using the ideal-gas law. At the normal pressure and at the temperature 273.16 K one cubic centimetre contains approximately 2.7×10^{19} molecules.

N₂, O₂, Ar. Under natural conditions air contains approximately 79% nitrogen, 20% oxygen and 1% argon (Junge, 1965), accordingly the concentration of N₂ should be $2.1 \times 10^{19} \text{ cm}^{-3}$, the concentration of O₂ should be $5.6 \times 10^{18} \text{ cm}^{-3}$ and the concentration of Ar should be $2.7 \times 10^{17} \text{ cm}^{-3}$

Kr, He. The natural concentrations of all rare gases have been taken from the work (Junge. 1965).

H₂O. The actual concentration of water depends strongly on the temperature. In the table 3.1 we can see the concentrations of water vapour in the air containing

Table 3.1. The dependence of water vapour on temperature.

temperature, K	243	273	303
pressure of the saturated water vapour, mb	0.5	6.1	42.6
concentration in the air containing 50% relative humidity, cm^{-3}	6.7×10^{15}	8.2×10^{16}	5.7×10^{17}

50% relative humidity, at the various temperatures (Tverskoi, 1962). In the present work we consider the concentration of $2.7 \times 10^{17} \text{ cm}^{-3}$ to be natural. This concentration corresponds approximately to the 50% relative humidity at the temperature 290 K or 17°C. It is necessary to point out, that a variation in the

temperature from -30°C to $+30^{\circ}\text{C}$ causes the concentration of water vapour to be changed by approximately 100 times (at the same relative humidity). Therefore, if we deal with the peculiarities of the evolution of ions, caused by a change in the temperature, the influence of the change in the concentration of water vapour is to be considered the main factor. The other factors, caused by the change in the temperature, e.g., possible variations in the rates of chemical reactions, are generally at least 10 times smaller as compared with the influence of the change in the concentration of water vapour.

CH₄. A lot of data is available about the concentration of methane. A sample is given as follows. According to the classic work (Junge, 1965) the concentrations of methane should be in the interval from $3.2 \times 10^{13} \text{ cm}^{-3}$ to $4.1 \times 10^{13} \text{ cm}^{-3}$; during long-time measurements in USA the mean value of $3.9 \times 10^{13} \text{ cm}^{-3}$ has been found out (Stephens, 1985). In the paper (Bonsang *et al.*, 1991) the concentrations of methane have been measured till a height of 1600 m, in accordance to those data the near-ground concentrations should be in the interval from $4.3 \times 10^{13} \text{ cm}^{-3}$ to $4.5 \times 10^{13} \text{ cm}^{-3}$; in accordance to the paper (Koropalov, 1988) the mean concentration of methane should be equal to $4.4 \times 10^{13} \text{ cm}^{-3}$. The concentrations near to the previous ones have been found out in Antarctic at heights of 6–12 km as well, corresponding data range between $4.1 \times 10^{13} \text{ cm}^{-3}$ and $4.6 \times 10^{13} \text{ cm}^{-3}$ (Heidt *et al.*, 1989).

As we can see, the concentrations of methane vary in quite confined limits only. In the present work we take the normal concentration equal to $4.0 \times 10^{13} \text{ cm}^{-3}$.

CO. As to the concentration of carbon monoxide, then the author of the present work has found some various information. According to the classic work (Junge, 1965) the concentrations of carbon monoxide should be in the interval from $2.7 \times 10^{11} \text{ cm}^{-3}$ to $5.4 \times 10^{12} \text{ cm}^{-3}$; the results of a comprehensive study show the mean concentration equal to $2.7 \times 10^{12} \text{ cm}^{-3}$, while in the polluted air the concentration can reach the value of $1.3 \times 10^{13} \text{ cm}^{-3}$ (Cicerone, 1988). In the Antarctic at heights 6–12 km the concentrations between $1.1 \times 10^{12} \text{ cm}^{-3}$ and $2.5 \times 10^{12} \text{ cm}^{-3}$ have been found out (Heidt *et al.*, 1989); a model shows concentrations in the interval between $9.5 \times 10^{11} \text{ cm}^{-3}$ and $5.0 \times 10^{12} \text{ cm}^{-3}$, while the concentrations should depend on the geographical latitude (Isaksen and Hov, 1987). However, some results showing higher concentrations can be pointed out as well: in accordance to the paper (Kuttler, 1984) the concentrations of carbon monoxide should range between $2.7 \times 10^{13} \text{ cm}^{-3}$ (in the case of unpolluted air) and $5.0 \times 10^{15} \text{ cm}^{-3}$ (in the case of polluted air). In the present work we regard the concentration of $3.0 \times 10^{12} \text{ cm}^{-3}$ as normal.

COS. The average concentration of carbonyl sulfide near the ground should be, in accordance to the results of measurements, $1.3 \times 10^{10} \text{ cm}^{-3}$ (Karol *et al.*, 1983); the mean value of the concentration of same gas in Arctic was found to be $1.5 \times 10^{10} \text{ cm}^{-3}$ (Hov *et al.*, 1984). The calculations in accordance with a photochemical model have given concentrations ranging between the values of $2.7 \times 10^9 \text{ cm}^{-3}$ and $1.4 \times 10^{10} \text{ cm}^{-3}$ (Sze and Malcolm, 1980). In the current work we regard the concentration of $1.3 \times 10^{10} \text{ cm}^{-3}$ as normal.

CO₂. According to the work (Junge, 1965) the mean concentration of carbon dioxide should be equal to $8.7 \times 10^{15} \text{ cm}^{-3}$. There is some difference between the

concentrations of carbon dioxide in case of polluted and in case of unpolluted regions, but the difference is not very essential: the concentrations of carbon dioxide range from $8.0 \times 10^{15} \text{ cm}^{-3}$ to $1.9 \times 10^{16} \text{ cm}^{-3}$ (Kuttler, 1984). In the present work we regard the concentration $9.0 \times 10^{15} \text{ cm}^{-3}$ as normal.

HCN. The data about the concentration of hydrogen cyanide have been looked over in the paper (Cicerone and Zellner, 1983). In the present work we accept the mean concentration presented in the mentioned paper, so we regard the concentration of $4.3 \times 10^9 \text{ cm}^{-3}$ as normal.

HNO₃. On the whole, the concentrations of nitric acid should range between the values of $2.7 \times 10^9 \text{ cm}^{-3}$ and $1.4 \times 10^{11} \text{ cm}^{-3}$ (Karol *et al.*, 1983); the measurements performed in England have shown concentrations ranging between the values of $1.4 \times 10^9 \text{ cm}^{-3}$ and $2.5 \times 10^{10} \text{ cm}^{-3}$ (Harrison and Allen, 1990). It seems as if the concentrations of nitric acid vary in quite large limits. In general, the concentrations tend to be smaller in the urban areas and larger in the rural areas; the respective concentrations can be frequently found in the intervals from $1.8 \times 10^9 \text{ cm}^{-3}$ to $9 \times 10^{10} \text{ cm}^{-3}$ and from $1.8 \times 10^9 \text{ cm}^{-3}$ to $3 \times 10^{10} \text{ cm}^{-3}$ (Grennfelt, 1980). Some results, near to the previous ones, have been found out also in the paper (Knop and Arnold, 1985), where the concentration of nitric acid has been studied mainly in the middle troposphere. Additionally, some results of comparisons between the results of measurements and the height variations of concentrations, in conformity with model calculations have been presented, in accordance to the results of comparisons the concentrations of nitric acid should range between the values of $5 \times 10^9 \text{ cm}^{-3}$ and $5 \times 10^{11} \text{ cm}^{-3}$, while the marine concentrations were, on the average, 10 times smaller. Some results, near to the previous ones have been found out also in the paper (Talbot *et al.*, 1990), in accordance to that paper the concentrations of nitric acid should be in the interval from $5 \times 10^9 \text{ cm}^{-3}$ to $5 \times 10^{10} \text{ cm}^{-3}$, while larger concentrations have been found more rarely.

In the present work we regard the concentration of $1.0 \times 10^{10} \text{ cm}^{-3}$ as normal.

H₂. According to the classic work (Junge, 1965) the concentrations of hydrogen should be in the interval from $1.1 \times 10^{13} \text{ cm}^{-3}$ to $2.7 \times 10^{13} \text{ cm}^{-3}$. Known measurements performed later have shown results near to the results mentioned above. All the known measurements have shown a comparatively limited variation in concentration of hydrogen. Here we refer to a comprehensive paper (Schmidt, 1978), which has shown the concentrations of hydrogen ranging between the values $1.5 \times 10^{13} \text{ cm}^{-3}$ and $1.57 \times 10^{13} \text{ cm}^{-3}$, while the measured concentrations were nearly equal both in marine and in land measurements. In the current work the concentration of $1.5 \times 10^{13} \text{ cm}^{-3}$ is considered normal.

H₂S. According to the classic work (Junge, 1965) the concentrations of H₂S should be in the interval from $5.4 \times 10^{10} \text{ cm}^{-3}$ to $5.4 \times 10^{11} \text{ cm}^{-3}$. On the other hand, the data differing from the ones mentioned last can be found out as well. In conformity with the paper (Sze and Malcolm, 1980), where the concentration of H₂S was studied by means of a photochemical model, the concentrations should range between $1.4 \times 10^8 \text{ cm}^{-3}$ and $8.6 \times 10^9 \text{ cm}^{-3}$. Nevertheless, the concentrations mentioned last match well with the results of measurements referred to in the paper (Sze and Malcolm, 1980). On the whole, known data show a comparatively wide variation in concentration of H₂S.

In the current work the concentration of $1.0 \times 10^{10} \text{ cm}^{-3}$ is considered normal. H_2SO_4 . The concentration of gas phase sulfuric acid can be estimated by means of an extrapolation of a height variation presented in the paper (Turco *et al.*, 1979). The near-ground concentration of sulfuric acid obtained in this way should be equal to $4 \times 10^8 \text{ cm}^{-3}$. The known results of measurements are obtained by virtue of a comparison of relative abundances of ions NO_3^- and ions H_2SO_4^- (Eisele and Tanner, 1993). According to the paper mentioned last the concentrations of sulfuric acid should range between $1.0 \times 10^5 \text{ cm}^{-3}$ (fog, night) and $2.0 \times 10^7 \text{ cm}^{-3}$ (day). H_2SO_4 should arise mainly by means of the reactions $\text{OH} + \text{SO}_2 \rightarrow \text{HSO}_3$, $\text{O}_2 + \text{HSO}_3 \rightarrow \text{SO}_3$, and $\text{H}_2\text{O} + \text{SO}_3 \rightarrow \text{H}_2\text{SO}_4$, and should disappear mainly by means of various processes leading to the generation of aerosol particles. (Eisele and Tanner, 1991).

In the present work we take the concentration of $4.0 \times 10^6 \text{ cm}^{-3}$ as normal. It is to be pointed out, that the model of negative ions is quite sensitive to the actual concentration of sulfuric acid. On the other hand, our knowledge about the actual concentration of gaseous sulfuric acid seems to be limited as shown above, therefore the fact has to be remembered, that the potential inaccuracy in the actual concentration of sulfuric acid will have a significant effect on the authenticity of the model.

NH_3 . As to the concentration of ammonia the data found out by the author of the present work is as follows: the measurements performed in England have shown concentrations of ammonia ranging between the values of $1.4 \times 10^9 \text{ cm}^{-3}$ and of $1.4 \times 10^{11} \text{ cm}^{-3}$ (Harrison and Allen, 1990); the paper (Ziereis and Arnold, 1986) has given a survey of known results of measurements, in conformity with which the concentrations of ammonia near the ground should be in the interval from $5 \times 10^9 \text{ cm}^{-3}$ to $2.7 \times 10^{11} \text{ cm}^{-3}$, whereas at the level about 1 km the concentrations were below $2.7 \times 10^{10} \text{ cm}^{-3}$. In the present work we regard the concentration of $1.0 \times 10^{10} \text{ cm}^{-3}$ as normal.

NO . The mean natural concentration of NO should be $1.0 \times 10^9 \text{ cm}^{-3}$, in the industrial areas concentrations can reach the values of about $3.0 \times 10^{10} \text{ cm}^{-3}$ (Karol *et al.*, 1983). Some measurements have shown concentrations exceeding the ones mentioned last, like this the concentration of NO can reach the approximate value of $5.0 \times 10^{12} \text{ cm}^{-3}$ (Sjödín and Ferm, 1985). In the current work the concentration of $5.0 \times 10^9 \text{ cm}^{-3}$ is considered normal.

NO_2 . The natural concentrations of NO_2 should be in the interval from $5.0 \times 10^9 \text{ cm}^{-3}$ to $7.0 \times 10^{10} \text{ cm}^{-3}$, in the polluted areas the concentrations can achieve the value of about $1.0 \times 10^{13} \text{ cm}^{-3}$ (Karol *et al.*, 1983). Some results, similar to the ones mentioned last have been found out also by other authors, in those papers the observed concentrations have ranged between $9 \times 10^{10} \text{ cm}^{-3}$ and $1.2 \times 10^{12} \text{ cm}^{-3}$ (Sjödín and Ferm, 1985), or between $5.2 \times 10^{10} \text{ cm}^{-3}$ and $2.9 \times 10^{11} \text{ cm}^{-3}$ (Kuttler, 1984). In the current work we regard the concentration of $7.0 \times 10^{10} \text{ cm}^{-3}$ as normal.

N_2O . According to the classic work (Junge, 1965) the concentrations of N_2O should be in the interval from $6.7 \times 10^{12} \text{ cm}^{-3}$ to $1.6 \times 10^{13} \text{ cm}^{-3}$. The more recent results of measurements have shown following concentrations: above the Antarctic the concentrations were in the interval from $7.2 \times 10^{12} \text{ cm}^{-3}$ to $8.2 \times 10^{12} \text{ cm}^{-3}$ (Heidt *et al.*, 1989), over the Pacific the mean concentration of 8.1×10^{12}

cm^{-3} has been observed (DeLorey *et al.*, 1988), in the Hawaii the mean concentration was $8.8 \times 10^{12} \text{ cm}^{-3}$ (Cicerone *et al.*, 1978). As it can be seen from the results mentioned above, the concentrations of N_2O vary in quite limited ranges only. Additionally, some attempts have been made to simulate the tropospheric concentrations of N_2O , the results of simulations have shown a significant accordance with the results of measurements. According to the results of simulations, the concentrations of N_2O should not depend on the altitude, at least in the range from 0 to 10 km, whereas the mean concentration should be equal to $7 \times 10^{12} \text{ cm}^{-3}$ (Golombek and Prinn, 1986). In the present work we consider the concentration of $8.0 \times 10^{12} \text{ cm}^{-3}$ normal.

O_3 . As to the classic work (Junge, 1965), the concentrations of ozone should be in the interval from zero to $1.4 \times 10^{12} \text{ cm}^{-3}$; the model presented in the paper (Isaksen and Hov, 1987) has shown concentrations depending on the geographical latitude ranging between the values of $7 \times 10^{11} \text{ cm}^{-3}$ and $1.5 \times 10^{12} \text{ cm}^{-3}$. Measurements performed in the forests of USA have shown the concentrations ranging from $5 \times 10^{11} \text{ cm}^{-3}$ to $3.2 \times 10^{12} \text{ cm}^{-3}$ (Whitby and Coffey, 1977), in a Swedish city the concentrations from $1.2 \times 10^{11} \text{ cm}^{-3}$ to $9 \times 10^{11} \text{ cm}^{-3}$ have been observed (Sjödín and Ferm, 1985). The concentrations of ozone do not depend on the altitude, at least up to the level of about 3 km, while the mean concentration is about $9.5 \times 10^{11} \text{ cm}^{-3}$ (Heikes *et al.*, 1987). The actual concentration of ozone should have a positive correlation with the actual concentrations of NO and CH_4 , since the considerable abundance of the tropospheric ozone should originate from CH_4 by means of reactions with NO (Fishman and Crutzen, 1977; Mitra, 1990). At the same time the actual concentration of ozone should have a negative correlation with the actual concentration of OH , since OH can be considered a sink for ozone (Fishman and Crutzen, 1977).

In the present work we consider the concentration of $1.0 \times 10^{12} \text{ cm}^{-3}$ normal.

SO_2 . According to the classic work (Junge, 1965) the concentrations of sulfur dioxide should be in the interval from zero to $5.4 \times 10^{11} \text{ cm}^{-3}$. The actual concentration depends on the amount of industry, in the meanly industrialized areas concentrations should range between $1.9 \times 10^{11} \text{ cm}^{-3}$ and $3.2 \times 10^{11} \text{ cm}^{-3}$ (Batcher and Charlson, 1984), the dependence on the industry has been confirmed also by the paper (Kuttler, 1984). In accordance with the paper mentioned last the concentrations of sulfur dioxide should range between $2 \times 10^9 \text{ cm}^{-3}$ and $3 \times 10^{10} \text{ cm}^{-3}$ (over the oceans), whereas in the industrial areas the concentrations can reach a value of about $5 \times 10^{13} \text{ cm}^{-3}$.

The concentrations of SO_2 depend, on the average, on the altitude. At an altitude of about 2 km the concentrations of SO_2 should be, on the average, about 10 times less abundant than the near-ground concentrations. Still, it is to be noted, that the dependences similar to the above-mentioned ones can not be met constantly (Heikes *et al.*, 1987).

In the current work we consider the concentration of $3.0 \times 10^{10} \text{ cm}^{-3}$ to be normal.

3.2. Gases containing halogen atoms

BrNO₂. The author of the present work could not find any data either about the results of measurements of concentrations or about the chemical reactions between the neutral compounds including BrNO₂, for that reason we have evaluated the concentration of BrNO₂ being equal to the concentration of ClNO₂, therefore we consider the concentration of $1.1 \times 10^9 \text{ cm}^{-3}$ to be the normal one; the note "estimated" has been added because of the lack of data.

CF₃. There is no direct data available about the concentration of CF₃. We have proceeded from the fact, that, compared to the known concentrations of stable molecules (CH₄, C₂H₆), the known concentrations of many radicals (CH₃, C₂H₅) are much less abundant. Since CF₃ is also a radical, we have evaluated the concentration of CF₃ being 1000 times smaller than the concentration of CF₄, therefore, we consider the concentration of $1.1 \times 10^6 \text{ cm}^{-3}$ normal; the note "estimated" has been added because of the lack of data.

CF₄. The concentrations of CF₄ have been measured only at altitudes starting from 2 km. At an altitude near 2 km the concentration should be about $1.9 \times 10^9 \text{ cm}^{-3}$ (Karol *et al.*, 1983), at an altitude near 10 km the concentration should be about $1.8 \times 10^9 \text{ cm}^{-3}$ (Fabian *et al.*, 1987). Hence, the concentrations of CF₄ do not show any significant dependence on the altitude. In the current work the concentration of $1.9 \times 10^9 \text{ cm}^{-3}$ comes to be considered normal.

CClF₃. There is no direct data available about the concentration of CClF₃, therefore, we have evaluated the concentration of CClF₃ being nearly equal to the concentration of CHF₃. The operation mentioned last can be motivated by the fact, that the known concentrations of many halogen compounds do not differ very much from one another, as it can be seen from the present survey. Hence, in the present work we regard the concentration of $2.2 \times 10^8 \text{ cm}^{-3}$ as normal; the note "estimated" has been added owing to the shortage of data.

CCl₂. There is no direct data available about the concentration of CCl₂. We have taken into consideration the fact, that the valency of carbon equal to 4 is more usual than the valency equal to 2. Proceeding from this, we have evaluated the concentration of CCl₂ being 100 times less than the concentration of CCl₄. Hence, in the present work we consider the concentration of $5.5 \times 10^7 \text{ cm}^{-3}$ normal; the note "estimated" has been added due to the shortage of data.

CCl₂F. It seems as if the molecules of radical CCl₂F mainly originate from the reactions of CHCl₂F with either OH or O (Atkinson *et al.*, 1989a; Atkinson *et al.*, 1989b; Baulch *et al.*, 1980). Nevertheless, any scheme of reactions sufficient for an estimate of steady-state concentration of CCl₂F can not be constructed because of the insufficiency of data. Therefore, we have taken into consideration the fact, that the known concentrations of many radicals are much smaller as compared with the known concentrations of stable molecules. In consequence of this we have assumed the concentration of CCl₂F being 100 times smaller than the concentration of CHCl₂F. Hence, in the present work we regard the concentration of $3.3 \times 10^6 \text{ cm}^{-3}$ as normal; the lack of data required the addition of the note "estimated"

CCl₂F₂. It seems as if the concentrations of freone-12 somewhat depend on the altitude: at an altitude about 2 km the mean concentration of $5.4 \times 10^9 \text{ cm}^{-3}$ has

been observed (Karol *et al.*, 1983), whereas long-time measurements performed at lower altitudes have shown the mean concentration equal to $8.1 \times 10^9 \text{ cm}^{-3}$ (Cunnold *et al.*, 1986). Some other data about the concentration of F-12 are also available: over the Pacific Ocean the mean concentration was $7.5 \times 10^9 \text{ cm}^{-3}$ (DeLorey *et al.*, 1988), in Arctic the concentrations have ranged between the values of $9.5 \times 10^9 \text{ cm}^{-3}$ and $9.6 \times 10^9 \text{ cm}^{-3}$ (Hov *et al.*, 1984). In the current work the concentration of $7.5 \times 10^9 \text{ cm}^{-3}$ is taken as normal.

CCl₃. The molecules of radical CCl₃ arise mainly by means of reactions between CCl₄ molecules and O atoms (Atkinson *et al.*, 1989a; Atkinson *et al.*, 1989b; Baulch *et al.*, 1980), but also as a result of dissociation of CCl₄ molecules, the respective rate constants have values of $3.5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ and $3.9 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ (Golombek and Prinn, 1986). On the other hand, nothing is known about the reactions that could be considered as sinks for CCl₃. Therefore, any scheme of reactions sufficient for an estimate of steady-state concentration of CCl₃ can not be constructed due to the insufficiency of data.

To get an estimate for the concentration of CCl₃ we have taken into consideration the fact, that the known concentrations of many radicals are often much less abundant as compared with the known concentrations of stable molecules. Next, we have assumed, that the ratio between the concentrations of CCl₃ and CCl₄ (on the one hand) is nearly equal to the ratio between the concentrations of CF₃ and CF₄ (on the other hand). For that reason we have assumed the concentration of CCl₃ being about 1000 times less than the concentration of CCl₄. Hence, in the present work we regard the concentration of $5.5 \times 10^6 \text{ cm}^{-3}$ as normal; the note "estimated" has been added by reason of the lack of data.

CCl₃F. The paper (Frank *et al.*, 1991), where the concentrations of freone-11 have been measured both under urban and rural conditions, has shown the concentration of F-11 ranging between $4.1 \times 10^9 \text{ cm}^{-3}$ and $4.1 \times 10^{10} \text{ cm}^{-3}$; other results obtained by long-time measurements have shown the mean concentration equal to $4.8 \times 10^9 \text{ cm}^{-3}$ (Cunnold *et al.*, 1986). Additionally, over the Pacific Ocean the mean concentration was $4.7 \times 10^9 \text{ cm}^{-3}$ (DeLorey *et al.*, 1988) and in Arctic the concentrations of F-11 were in the interval from $5.2 \times 10^9 \text{ cm}^{-3}$ to $5.6 \times 10^9 \text{ cm}^{-3}$ (Hov *et al.*, 1984).

Some results obtained at higher levels have shown concentrations being a bit lower as compared to the concentrations obtained at near-ground levels. The concentrations of F-11 at altitudes from 2 to 12 km should be, on the average, $3.2 \times 10^9 \text{ cm}^{-3}$ (Fraser and Pearman, 1978) or range between $3.0 \times 10^9 \text{ cm}^{-3}$ and $4.6 \times 10^9 \text{ cm}^{-3}$ (Fraser and Pearman, 1983).

In the present work we consider the concentration $5.0 \times 10^9 \text{ cm}^{-3}$ normal.

CCl₄. It looks as if the concentrations of CCl₄ depend on the amount of industry: the measurements performed in Los Angeles have shown the mean concentration equal to $1.4 \times 10^{11} \text{ cm}^{-3}$ (Karol *et al.*, 1983); whereas the results obtained in Arctic have shown the mean concentration of $3.0 \times 10^9 \text{ cm}^{-3}$ (Hov *et al.*, 1984); in accordance with the results obtained over the Pacific Ocean the mean concentration of CCl₄ should be equal to $4.0 \times 10^9 \text{ cm}^{-3}$ (DeLorey *et al.*, 1988) or $4.6 \times 10^9 \text{ cm}^{-3}$ (Koropalov, 1988). The paper (Frank *et al.*, 1991), in which the concentrations of CCl₄ have been measured both under urban and rural

conditions, has shown the concentration of CCl_4 ranging between $1.1 \times 10^{10} \text{ cm}^{-3}$ and $1.1 \times 10^{11} \text{ cm}^{-3}$. The concentrations of CCl_4 do not show any significant dependence on the altitude: the results of measurements obtained during 12 months at levels from 2 km to 12 km have shown the mean concentration of $4.3 \times 10^9 \text{ cm}^{-3}$ (Fraser and Pearman, 1978). In the present work we regard the concentration of $5.0 \times 10^9 \text{ cm}^{-3}$ as normal.

CHCIF. There is no direct data available about the concentration of CHCIF. To get an estimate for the concentration of CHCIF we have taken into consideration the fact, that the known concentrations of many radicals are often much lower as compared with the known concentrations of stable molecules. Now the stable molecules of interest are either CHClF_2 or CHCl_2F , whereas the known concentrations of both gases are nearly equal to each other. Next, we have assumed the molecules of CHCIF being about 1000 times less abundant than the molecules of CHCl_2F are. Accordingly, in the present work we consider the concentration of $1.1 \times 10^6 \text{ cm}^{-3}$ normal; the note "estimated" has been added because of the shortage of data.

CHCIF₂. The tropospheric concentration of freone-22 should be, on the average, $1.4 \times 10^9 \text{ cm}^{-3}$ (Brasje *et al.*, 1987). In the present work we consider the concentration of $1.4 \times 10^9 \text{ cm}^{-3}$ normal; the note "estimated" has been added because of the shortage of direct results of measurements.

CHCl₂. To get an estimate for the concentration of radical CHCl_2 we have used a method similar to that used in case of CHCIF. Now we have assumed the molecules of CHCl_2 being about 1000 times less abundant than the molecules of CHCl_3 . Accordingly, in the present work the concentration of $5.5 \times 10^6 \text{ cm}^{-3}$ is considered to be normal; the note "estimated" has been added because of the shortage of data.

CHCl₂F. The concentration of CHCl_2F has been measured at an altitude of about 2.5 km; the mean concentration of $3.8 \times 10^8 \text{ cm}^{-3}$ has been found out (Karol *et al.*, 1983). Herein we accept the results of the work mentioned last and regard the concentration of $3.8 \times 10^8 \text{ cm}^{-3}$ as normal.

CHCl₃. About the concentration of chloroform author of present work has found the data mentioned below: the measurements performed in Arctic have shown concentrations ranging between the $4.5 \times 10^8 \text{ cm}^{-3}$ and $7.2 \times 10^8 \text{ cm}^{-3}$ (Hov *et al.*, 1984); the paper (Frank *et al.*, 1991), where the concentrations of chloroform have been measured both under urban and rural conditions, has shown the concentrations of chloroform ranging between $4.8 \times 10^8 \text{ cm}^{-3}$ and $4.8 \times 10^{10} \text{ cm}^{-3}$. It seems as if the concentrations of chloroform tend to depend on the altitude: the results of measurements obtained at heights of 4–14 km have shown the concentrations being in the interval from $1.6 \times 10^8 \text{ cm}^{-3}$ to $3.2 \times 10^8 \text{ cm}^{-3}$ (Cronn *et al.*, 1977). In the present work we consider the concentration of $5.0 \times 10^9 \text{ cm}^{-3}$ normal.

CHF₂. The author of the present work has not found any data about the concentration of CHF_2 . To get an estimate for the concentration of radical CHF_2 after all we have used the assumption about the concentrations of radicals. The similar method has been used often in this work, e.g. by the CHCIF. Now we have assumed the molecules of CHF_2 being about 1000 times less abundant than the molecules of CHF_3 . Accordingly, in the present work we regard the

concentration of $2.2 \times 10^5 \text{ cm}^{-3}$ as normal; the note "estimated" has been added because of the shortage of data.

CHF₃. There is no direct data available about the concentration of CHF₃. Therefore, to get an estimate we have evaluated the concentration of CHF₃ being nearly equal to the concentration of CH₃F. This assumption can be motivated by the fact, that the known concentrations of many halogen compounds do not differ very much from one another, as it can be seen from the current survey. Hence, in the present work we consider the concentration of $2.2 \times 10^8 \text{ cm}^{-3}$ normal; the note "estimated" has been added owing to the shortage of data.

CH₂Br. There is no direct data available about the concentration of radical CH₂Br. In order to get an estimate, we have assumed, that the ratio between the concentrations of CH₂Br and CH₃Br nearly equals the ratio between the concentrations of CH₂Cl and CH₃Cl. Hence, in the present work we regard the concentration of $4.4 \times 10^5 \text{ cm}^{-3}$ as normal; the note "estimated" has been added by reason of the lack of data.

CH₂Cl. Radical CH₂Cl arises mainly by means of reactions between methyl chloride and OH (Atkinson *et al.*, 1989a; Atkinson *et al.*, 1989b; Baulch *et al.*, 1980). Nevertheless, by means of the last-mentioned-data any scheme of reactions can not be constructed. As a result of this, we have to use some assumptions. We have taken the assumption, that the concentration of the radical should be about 1000 times smaller as compared with the concentration of methyl chloride. This way we have got the concentration of $2.2 \times 10^7 \text{ cm}^{-3}$ which is considered normal in the present work. The note "estimated" has been added by reason of the shortage of data.

CH₂F. There is no direct data available about the concentration of radical CH₂F. To get an estimate, we have followed the method which was used e.g. in case of the radical CH₂Br. Now we have assumed, that the ratio between the concentrations of CH₂F and CH₃F, on the one hand, is nearly equal to the ratio between the concentrations of CH₂Cl and CH₃Cl, on the other hand. Hence, in the present work we regard the concentration of $2.2 \times 10^5 \text{ cm}^{-3}$ as normal; the note "estimated" has been added due to the lack of data.

CH₂Cl₂. The concentration of CH₂Cl₂ has been measured in Arctic, the observed mean concentration was $2.1 \times 10^9 \text{ cm}^{-3}$ (Hov *et al.*, 1984). In the present work we accept the results mentioned last, hence, we regard the concentration of $2.1 \times 10^9 \text{ cm}^{-3}$ as normal.

CH₂F₂. There is no direct data available about the concentration of CH₂F₂, in consequence of which the concentration of CH₂F₂ should be nearly equal to the concentration of CH₂Cl₂. Hence, in the present work we regard the concentration of $2.2 \times 10^9 \text{ cm}^{-3}$ as normal; the note "estimated" has been added because of the shortage of data.

CH₃Br. The concentration of CH₃Br has been measured in Arctic, the observed mean concentration was $3.9 \times 10^8 \text{ cm}^{-3}$ (Hov *et al.*, 1984). In the present work we accept the last mentioned results, hence, the concentration of $3.9 \times 10^8 \text{ cm}^{-3}$ is taken as normal.

CH₃Cl. It looks as if the concentrations of methyl chloride do not depend on the altitude: the results obtained in Arctic have shown the mean concentration of $2.0 \times 10^{10} \text{ cm}^{-3}$ (Hov *et al.*, 1984); in accordance with the measurements

performed in Western Europe concentrations of methyl chloride should range between $1.0 \times 10^{10} \text{ cm}^{-3}$ and $4.0 \times 10^{10} \text{ cm}^{-3}$ (Tille *et al.* 1985), whereas the results obtained at a level of about 2.5 km have shown the mean concentration equal to $1.9 \times 10^{10} \text{ cm}^{-3}$ (Karol *et al.*, 1983). In the present work we regard the concentration of $2.2 \times 10^{10} \text{ cm}^{-3}$ as normal.

CH₃F. There is no direct data available about the concentration of methyl fluoride. In consequence of what we have assumed, the concentration of methyl fluoride should be nearly equal to the concentration of methyl chloride. Additionally, we have taken into account the chemical activity of methyl fluoride, which should exceed the activity of the methyl chloride. As a higher chemical activity should result in a decrease of the steady-state concentration, in the current work we consider the concentration of $2.2 \times 10^8 \text{ cm}^{-3}$ normal; the note "estimated" has been added because of the shortage of data.

C₂F₄. There is no direct data available about the concentration of C₂F₄, owing to what we presume that the concentration of C₂F₄ is to be nearly equal to the concentration of C₂Cl₄ in the present work. Unlike the concentration of C₂F₄, the concentration of C₂Cl₄ has been measured; the concentration of C₂Cl₄ should range between $3 \times 10^8 \text{ cm}^{-3}$ and $1.7 \times 10^{11} \text{ cm}^{-3}$ (Frank *et al.*, 1991); whereas the mean value for the concentration of C₂Cl₄ should be $1.1 \times 10^9 \text{ cm}^{-3}$ (Koropalov, 1988). That is why, in the present work we regard the concentration of $1.1 \times 10^9 \text{ cm}^{-3}$ as normal; the note "estimated" has been added due to the shortage of data.

C₂F₅. There is no direct data available about the concentration of C₂F₅. Since C₂F₅ is a radical, we have assumed it being about 1000 times less abundant as compared with the known abundance of stable molecules of C₂F₆. Thus, in the present work we consider the concentration of $1.1 \times 10^5 \text{ cm}^{-3}$ normal; the note "estimated" has been added because of the shortage of data.

C₂F₆. The concentrations of C₂F₆ have been measured only at higher levels: in the paper (Fabian *et al.*, 1987) the dependence of concentrations on the altitude has been observed, while at a level of about 10 km the mean concentration was $5.4 \times 10^7 \text{ cm}^{-3}$; at some kilometers above the ground the mean concentration was about $1.1 \times 10^8 \text{ cm}^{-3}$ (Karol *et al.*, 1983). The major sources of C₂F₆ are obviously connected with human activity. Therefore it can be assumed that decrease in the altitude causes an increase in the concentration. Thus, in the current work the concentration of $2.0 \times 10^8 \text{ cm}^{-3}$ is considered normal.

C₂HF₃. There is no direct data available about the concentration of C₂HF₃, and that is why we assume the concentration of C₂HF₃ being nearly equal to the concentration of C₂HCl₃. Unlike the concentration of C₂HF₃, there are some data available about the concentration of C₂HCl₃: the concentration of C₂HCl₃ should range between $4.3 \times 10^8 \text{ cm}^{-3}$ and $8.6 \times 10^{10} \text{ cm}^{-3}$ (Frank *et al.*, 1991). Thus, in the present work we regard the concentration of $3.3 \times 10^9 \text{ cm}^{-3}$ as normal; the note "estimated" has been added due to the lack of data.

C₂H₂F₂. In the present work we assume the concentration of C₂H₂F₂ being nearly equal to the concentration of C₂H₂Br₂. The concentration of C₂H₂Br₂ has been measured in the urban air, it ranged between $3 \times 10^6 \text{ cm}^{-3}$ and $5.3 \times 10^8 \text{ cm}^{-3}$, whereas near garages the observed concentrations were in interval from $3.7 \times 10^6 \text{ cm}^{-3}$ to $5.6 \times 10^9 \text{ cm}^{-3}$ (Leinster *et al.*, 1978). Thus, in the present work we

consider the concentration of $3.3 \times 10^8 \text{ cm}^{-3}$ normal; the note “estimated” has been added due to the lack of data.

C₂H₂Cl₂. In the present work we presume the concentration of C₂H₂Cl₂ being nearly equal to the concentration of C₂H₂F₂. Consequently we regard the concentration of $3.3 \times 10^8 \text{ cm}^{-3}$ as normal one; the note “estimated” has been added because of the shortage of data.

C₂H₃F, C₂H₃Cl. There is no data available about the concentrations of either C₂H₃F or C₂H₃Cl. Owing to that we have to make some assumptions about the concentrations. And so, in the present work we consider the natural concentrations of C₂H₃F and C₂H₃Cl being equal to the known concentration of C₂H₂Cl₂, that results in the concentration of $3.3 \times 10^8 \text{ cm}^{-3}$; the note “estimated” has been added due to the lack of data.

C₂H₄F. There is no data available about the concentrations of C₂H₄F. In the present work we assume C₂H₄F (radical) being nearly 1000 times less abundant than C₂H₅F (stable molecule). Next, we assume the concentration of C₂H₅F being nearly equal to the known concentration of C₂H₅Cl. Thus, in the present work the concentration of $1.1 \times 10^5 \text{ cm}^{-3}$ is taken as normal; the note “estimated” has been added because of the shortage of data.

C₂H₅Cl. The concentrations of C₂H₅Cl have been measured at an altitude of about 1 km, the mean concentration equal to $1.1 \times 10^8 \text{ cm}^{-3}$ has been observed (Karol *et al.*, 1983). In the present work we accept the results mentioned last, thus, we consider the concentration of $1.1 \times 10^8 \text{ cm}^{-3}$ normal.

C₃F₈. There is no data available about the concentrations of C₃F₈. To get an estimate, we scan the known concentrations of CF₄ and C₂F₆. The natural concentration of CF₄ is considered to be equal to $1.9 \times 10^9 \text{ cm}^{-3}$, the natural concentration of C₂F₆ should be equal to $1.1 \times 10^8 \text{ cm}^{-3}$. As we can see, the concentration of C₂F₆ is nearly 10 times smaller, compared to the concentration of CF₄. And so, we assume C₃F₈ being also 10 times less abundant than C₂F₆ is. The concentration of C₃F₈ obtains the value of $1.1 \times 10^7 \text{ cm}^{-3}$, which is considered normal in the present work; the note “estimated” has been added due to the lack of data.

C₃H₄F. There is no data available about the concentrations of C₃H₄F. We suppose the concentration of C₃H₄F being somewhat close to the estimated concentration of C₂H₄F. Next, we take into consideration the fact, that the heavier molecules are often less abundant as compared with the similar, but lighter ones (e.g., see C₃F₈). Consequently, we should evaluate C₃H₄F being less abundant than C₂H₄F is. Thus, in the present work we regard the concentration of $5.5 \times 10^4 \text{ cm}^{-3}$ as normal one; the note “estimated” has been added because of the shortage of data.

C₆H₄F₂. There is no data available about the concentrations of C₆H₄F₂. Nevertheless, in conformity with the survey presented in the paper (Kelly *et al.*, 1994) concentrations of C₆H₄Cl₂ should not exceed the detection limit. The concrete detection limits depend on the methods used but they are often about 0.1 pptv. Next, we assume the concentrations of C₆H₄F₂ being nearly equal to the concentrations of C₆H₄Cl₂. The concentration of C₆H₄F₂ obtains the value of $2.2 \times 10^6 \text{ cm}^{-3}$, which is considered to be normal in the current work; the note “estimated” has been added because of the shortage of data.

CINO₂. There is no results of measurements available about the concentrations of CINO₂, still, some data about the reactions including CINO₂ molecules can be found. Using the data about chemical reactions, the scheme of reactions

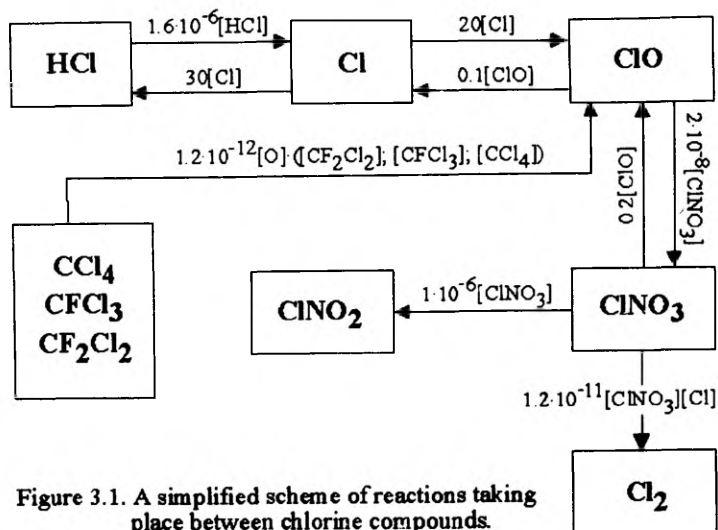


Figure 3.1. A simplified scheme of reactions taking place between chlorine compounds.

presented in the Figure 3.1 can be constructed. Next we examine the Figure 3.1. As the concentration of Cl should be comparatively low (see the discussion about the concentration of ClO), the majority of CINO₃ molecules should be transformed into CINO₂ molecules. According to the data reported in the paper (Mitra, 1990), the ratio between the concentrations of CINO₂ and CINO₃ should be nearly equal to the ratio between the concentrations of NO and NO₂, therefore the concentrations of CINO₂ should be lower than CINO₃ concentrations, but the difference should not be very essential. In accordance with the Figure 3.1, CINO₃ should be about 5×10^4 times more abundant than HCl. Consequently, both CINO₃ and CINO₂ should be quite abundant, and respective concentrations should be about $5 \times 10^{14} \text{ cm}^{-3}$, which is valid while presuming the absence of other sinks of CINO₃ or CINO₂. In any case, in conformity with the works (Atkinson *et al.*, 1989a; Atkinson *et al.*, 1989b; Baulch *et al.*, 1980; Schofield, 1973) it should not be any chemical reactions which could be considered sinks of CINO₃ or CINO₂. Although CINO₂ can be considered to be a stabile molecule, it is not reasonable to assume the concentration of it being comparable to the concentrations of main compounds of troposphere, such as CO₂, N₂O or H₂. If the concentrations of CINO₂ were comparable to the concentrations of main compounds of troposphere, it would be incomprehensible why CINO₂ has not been observed in the troposphere. Thus, we consider the concentration of CINO₂ being comparable to the concentrations of compounds such as H₂O₂. In consequence of this, the concentration of $1.1 \times 10^9 \text{ cm}^{-3}$ comes to be considered normal; the note “estimated” has been added due to the shortage of data.

ClO. There is no results of measurements available about the concentrations of ClO, but some data about the reactions including ClO molecules can be found out (Atkinson *et al.*, 1989a; Atkinson *et al.*, 1989b; Baulch *et al.*, 1980). Using

the data about chemical reactions the simplified scheme of reactions presented in the Figure 3.1 can be constructed. Any further study of chemical processes embracing ClO molecules has not been performed, only the data presented by the works mentioned last have been used. Next we examine the Figure 3.1.

As it can be seen on the Figure 3.1, the steady-state concentrations of almost all compounds (except for Cl₂, CCl₄, CFCl₃ and CF₂Cl₂) can be found out by means of the system of linear equations. Yet, we do not follow this line as the data employed by the scheme presented on the Figure 3.1 can be quite approximate. Therefore a rough estimate is a maximum that can be set as a purpose. For that goal, it is sufficient to evaluate the values of ratios between the abundances of ClO and HCl, and between those of ClNO₃ and HCl, at which HCl can be considered to be the gas abundance of which is quite well known. Accordingly, first we get $[Cl] \approx 10^{-7} [HCl]$, next $[ClO] \approx 1000 [Cl]$, or $[ClO] \approx 10^{-4} [HCl]$, finally we obtain $[ClNO_3] \approx 5 \times 10^8 [ClO]$, or $[ClNO_3] \approx 5 \times 10^4 [HCl]$. Thus, following the approximations presented above we obtain the concentration of ClO to be equal to $1.1 \times 10^6 \text{ cm}^{-3}$, concentration of which is considered normal in the present work; the note "estimated" has been added due to lack of data.

Cl₂. According to the work (Junge, 1965) the summary concentration of all chlorine compounds should range between $8.1 \times 10^9 \text{ cm}^{-3}$ and $4.1 \times 10^{10} \text{ cm}^{-3}$. We consider the concentration of Cl₂ to be nearly equal to the known concentration of HCl. Thus, in the present work we regard the concentration of $1.2 \times 10^{10} \text{ cm}^{-3}$ as normal; the note "estimated" has been added because of the shortage of data.

Cl₂O. There are neither no results of measurements of the concentrations of Cl₂O nor data about chemical reactions including molecules of Cl₂O available. Therefore quite low concentrations can be assumed. On the other hand, the absence of data about sinks indicates to the possibility of notable concentrations, which would be realized in case of presence of some sources of Cl₂O. Additionally, Cl₂O is a stabile compound, not a radical one. For that reason we assume the concentrations of Cl₂O to be somewhat lower as compared with the known concentrations which are near the detection limits. Thus, in the present work we consider the concentration of $1.1 \times 10^8 \text{ cm}^{-3}$ to be normal; the note "estimated" has been added due to the shortage of data.

F. There are no results of measurements available about the concentrations of F. It looks as if the concentration of F is quite low for, in accordance with the available data about the chemical reactions embracing F, F atoms should arise only from the slow reactions $FO+O \rightarrow O_2+F$ and $HF+O \rightarrow F+OH$, whilst the reaction $F+O_2+N_2 \rightarrow \text{products}$ works as a very effective sink for F (Atkinson *et al.*, 1989a; Atkinson *et al.*, 1989b; Baulch *et al.*, 1980). Because of the presence of the very effective sink the steady-state concentration of F can not be high, considering that we assume the concentration of F to be comparable to the concentration of H. Thus, in the present work we regard the concentration of $1.1 \times 10^3 \text{ cm}^{-3}$ as normal; the note "estimated" has been added due to the lack of data.

FNO₂. We assume the concentration of FNO₂ to be comparable to the concentration of ClNO₂. Additionally, we take into consideration the fact that the compounds including some atoms of fluorine are often more active, compared to the compounds consisting atoms of chlorine. As a higher chemical activity should

result in a decrease of the steady-state concentration, we consider the concentration of $1.1 \times 10^9 \text{ cm}^{-3}$ normal in the current work; the note "estimated" has been added by reason of the lack of data.

HBr. The concentrations of hydrogen bromide have been measured at an altitude of about 5 km, and the mean concentration equal to $4.1 \times 10^7 \text{ cm}^{-3}$ has been observed (Karol *et al.*, 1983). In the present work we accept these results, and consider the concentration of $4.1 \times 10^7 \text{ cm}^{-3}$ to be normal.

HCl. The concentrations of hydrogen chloride have been measured at various altitudes, but the observed concentrations show no significant dependence on the altitude: at an altitude of about 5 km the concentrations obtained the values ranging between $2.7 \times 10^9 \text{ cm}^{-3}$ and $2.7 \times 10^{10} \text{ cm}^{-3}$ (Karol *et al.*, 1983), at altitudes below 3 km the concentrations have ranged between $5.4 \times 10^8 \text{ cm}^{-3}$ and $1.4 \times 10^{10} \text{ cm}^{-3}$ (Vierkorn-Rudolph *et al.*, 1984), whereas the near-ground measurements performed in England have shown concentrations ranging from $1.6 \times 10^9 \text{ cm}^{-3}$ to $4.6 \times 10^{10} \text{ cm}^{-3}$ (Harrison and Allen, 1990). Likewise, a model describing marine concentrations of HCl is known, the respective mean concentration should be equal to $2.5 \times 10^{10} \text{ cm}^{-3}$ (Donahue and Prinn, 1990). In the current work the concentration of $1.2 \times 10^{10} \text{ cm}^{-3}$ is considered normal.

HF. We assume the concentrations of hydrogen fluoride to be comparable to the concentrations of hydrogen bromide. Additionally, we take into consideration the fact that, compared to the compounds consisting atoms of bromine, the compounds including some atoms of fluorine are often more active. As a higher chemical activity should result in a decrease of the steady-state concentration, HF should be somewhat less abundant as compared with the abundance of HBr. Thus, in the present work we consider the concentration of $4.4 \times 10^6 \text{ cm}^{-3}$ to be normal; the note "estimated" has been added owing to the shortage of data.

SF₃. We have taken into consideration the fact that, compared to the known concentrations of stable molecules, the known concentrations of many radicals are less abundant. Since SF₃ is also a radical, we have evaluated the SF₃ to be 10 times less abundant as compared with the abundance of SF₄. Now we have confined ourselves only to the ratio equal to 10, because of the quite low concentration of SF₄. Therefore, in the present work we consider the concentration of $1.1 \times 10^6 \text{ cm}^{-3}$ normal; the note "estimated" has been added by reason of the lack of data.

SF₄. There are neither any results of measurements about the concentrations of SF₄ nor any data about chemical reactions embracing the molecules of SF₄ available. Therefore, comparatively low concentrations can be assumed. On the other hand, valency of sulphur equal to 4 is energetically more useful than the valency equal to 6 (Knorre *et al.*, 1990). Therefore there is no reason to consider SF₄ to be less abundant as compared with the known abundance of SF₆. Thus, in the present work we consider the both concentrations to be nearly equal, obtaining the concentration equal to $1.1 \times 10^7 \text{ cm}^{-3}$. This concentration is considered normal; the note "estimated" has been added because of the shortage of data.

SF₅. We have taken into consideration the fact, that the known concentrations of many radicals (CH₃, C₂H₅) are less abundant as compared with the known concentrations of stable molecules (CH₄, C₂H₆). Since SF₅ is also a radical, we

have evaluated SF₅ to be 10 times less abundant if compared to the abundance of SF₆. Now we have confined ourselves only to the ratio equal to 10, because of the low concentration of SF₆. Thus, in the present work we consider the concentration of $1.1 \times 10^6 \text{ cm}^{-3}$ to be normal; the note "estimated" has been added due to the lack of data.

SF₆. The concentrations of SF₆ have been measured at various altitudes, the observed concentrations show no significant dependence on the altitude: the measurements performed at altitudes of about 10 km have given a result in the mean concentration which equals $8 \times 10^6 \text{ cm}^{-3}$ (Krey *et al.*, 1977), other measurements have shown mean concentrations close to those mentioned last: $5.4 \times 10^6 \text{ cm}^{-3}$ (Karol *et al.*, 1983), or $1.9 \times 10^7 \text{ cm}^{-3}$ (Michio and Muramatsu, 1986). In the present work we consider the concentration of $1.0 \times 10^7 \text{ cm}^{-3}$ normal.

3.3. Hydrocarbons and their derivatives

CH, CH₂. There are neither no results of measurements about the concentrations of these radicals nor any data about chemical reactions including molecules of these radicals available. We assume these radicals to be nearly 10 times less abundant as compared with the abundance of CH₃. Thus, in the present work we consider the concentration of $1.1 \times 10^3 \text{ cm}^{-3}$ to be normal; the note "estimated" has been added due to the lack of data.

CH₃. The steady-state concentration of the radical CH₃ can be estimated by means of known data about the chemical reactions. The main source of CH₃ should be the reaction $\text{OH} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}_2\text{O}$, the main sink should be the reaction $\text{O}_2 + \text{CH}_3 \rightarrow \text{CH}_3\text{O}_2$ (Donahue and Prinn, 1990). According to the presented rate constants, correspondingly $2.4 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ and $1.8 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, on the one hand, and in respect of the known concentrations of OH and CH₄, on the other hand, the steady-state concentrations of CH₃ should not exceed the value of some hundred molecules per cubic centimeter. Nevertheless, there are some supplementary reactions which can be considered as additional sources of CH₃ in addition to the reaction mentioned above. It is possible, that the additional reactions increase somewhat the actual concentration of CH₃. Hence, in the present work we consider the concentration of CH₃ to be nearly equal to the concentration of N, obtaining the concentration which equals $1.3 \times 10^4 \text{ cm}^{-3}$. This concentration is considered normal in the present work; the note "estimated" has been added because of the shortage of data.

C₂H. We proceed from the fact, that the known concentrations of many radicals (CH₃, C₂H₅) are less abundant while compared to the known concentrations of stable molecules (CH₄, C₂H₆). Since C₂H is also a radical, we have evaluated C₂H to be 1000 times less abundant as compared with the abundance of C₂H₂. Thus, in the present work we consider the concentration of $1.6 \times 10^7 \text{ cm}^{-3}$ to be normal; the note "estimated" has been added due to the lack of data.

C₂H₂. There is a lot of data available about the concentrations of acetylene. For example, the paper (Rudolph *et al.*, 1984a) has reported the shape of dependence of concentrations of acetylene on altitude, in accordance with the reported data in the whole troposphere mean concentration of acetylene should be equal to $1.6 \times 10^{10} \text{ cm}^{-3}$. In Arctic the measured concentrations have ranged from $1.8 \times 10^9 \text{ cm}^{-3}$ to $2.6 \times 10^{10} \text{ cm}^{-3}$ (Hov *et al.*, 1984), the marine concentrations have been

between $5.4 \times 10^8 \text{ cm}^{-3}$ and $6 \times 10^9 \text{ cm}^{-3}$ (Hov *et al.*, 1984), whereas in the coastal regions of Norway and Ireland the concentrations ranging between $2.7 \times 10^9 \text{ cm}^{-3}$ and $2.2 \times 10^{10} \text{ cm}^{-3}$ have been observed (Tille *et al.*, 1985). In the paper (Whitby and Altwicker, 1978), the results of the study of data available about the concentrations of acetylene have shown a dependence of concentrations of acetylene on the amount of industry. The urban concentrations can reach values of about $2.7 \times 10^{12} \text{ cm}^{-3}$. On the whole, the measured concentrations have not reached such values yet: in England the concentrations between $1.4 \times 10^{10} \text{ cm}^{-3}$ and $3.0 \times 10^{11} \text{ cm}^{-3}$ have been found out (Colbeck and Harrison, 1985), in India the concentrations range between $5.0 \times 10^9 \text{ cm}^{-3}$ and $3.0 \times 10^{11} \text{ cm}^{-3}$ (Mohan Rao and Pandit, 1988), the results observed over England at a level of about 2 km have shown the concentrations ranging between $3.0 \times 10^9 \text{ cm}^{-3}$ and $3.7 \times 10^{10} \text{ cm}^{-3}$ (Lightman *et al.*, 1990). Notably high concentrations have been observed in Los Angeles air only, namely ranging between $7.0 \times 10^{11} \text{ cm}^{-3}$ and $2.5 \times 10^{12} \text{ cm}^{-3}$ (Grosjean and Kochy, 1984). In the current work the concentration of $1.6 \times 10^{10} \text{ cm}^{-3}$ is considered normal.

C₂H₃. There is no data available about the concentrations of C₂H₃. Therefore, we proceed from the fact, that the known concentrations of many radicals (CH₃, C₂H₅) are less abundant as compared with the known concentrations of stable molecules (CH₄, C₂H₆). Since C₂H₃ is also a radical, we have evaluated C₂H₃ to be 1000 times less abundant as compared with that of C₂H₄. Thus, in the present work we consider the concentration $3.0 \times 10^7 \text{ cm}^{-3}$ normal; the note "estimated" has been added because of the shortage of data.

C₂H₄. It seems as if the concentrations of ethene behave somewhat like the concentrations of acetylene: both gases tend to be less abundant in the rural regions, and more abundant in the urban regions. The observed land concentrations have ranged between the values of $8.0 \times 10^9 \text{ cm}^{-3}$ and $1.1 \times 10^{12} \text{ cm}^{-3}$ (Puxbaum *et al.*, 1988; Colbeck and Harrison, 1985). The marine concentrations have been somewhat lower, ranging between $4.0 \times 10^9 \text{ cm}^{-3}$ and $1.2 \times 10^{11} \text{ cm}^{-3}$ (Bonsang *et al.*, 1991), whereas in Arctic the mean concentration equal to $2.0 \times 10^9 \text{ cm}^{-3}$ has been observed (Rasmussen *et al.*, 1983). In the city ethene can be more abundant: concentrations can reach values about of $2.4 \times 10^{12} \text{ cm}^{-3}$ (Grosjean and Kochy, 1984). In the present work we consider the concentration of $3.0 \times 10^{10} \text{ cm}^{-3}$ to be normal.

C₂H₅. The molecules of radical C₂H₅ arise mainly by means of reaction $\text{C}_2\text{H}_6 + \text{OH} \rightarrow \text{C}_2\text{H}_5$, whereas the main sink for molecules C₂H₅ should be the reaction $\text{C}_2\text{H}_5 + \text{O}_2 \rightarrow \text{C}_2\text{H}_5\text{O}_2$ (Lightman *et al.*, 1990). The rate constants of the reactions mentioned last have been presented in the paper (Donahue and Prinn, 1990), the respective rate constants should be $1.4 \times 10^{-17} \text{ cm}^3\text{s}^{-1}$ and $5 \times 10^{-12} \text{ cm}^3\text{s}^{-1}$. On the other hand, following the results of paper (Carney and Fishman, 1986), the rate constant of the first reaction should be equal to $1.9 \times 10^{-11} \text{ cm}^3\text{s}^{-1}$.

In case we proceed from the results of paper (Donahue and Prinn, 1990), the reaction decreasing the concentration of C₂H₅ is much faster as compared with the reaction producing C₂H₅ because of the large difference between both the rate constants and the concentrations of O₂ and OH. In this case the steady-state concentrations of C₂H₅ should be almost negligible. In case we proceed from the paper (Carney and Fishman, 1986), the situation somewhat changes, but the

steady-state concentrations of C_2H_5 remain very low. Therefore, in this work we assume the concentrations of C_2H_5 to be nearly equal to the concentrations of atomic hydrogen. In this way we obtain the concentration of $1.1 \times 10^3 \text{ cm}^{-3}$, which is considered normal. The note "estimated" has been added because of the lack of data.

C_2H_6 . It looks as if the concentrations of ethane behave alike the concentrations of acetylene: both gases tend to be less abundant in the rural regions, and more abundant in the urban ones. The observed land concentrations have ranged between the values of $1.5 \times 10^{10} \text{ cm}^{-3}$ and $1.5 \times 10^{12} \text{ cm}^{-3}$ (Tille *et al.*, 1985; Colbeck and Harrison, 1985), whereas in the city the concentrations can reach values of about $5.9 \times 10^{12} \text{ cm}^{-3}$ (Grosjean and Kochy, 1984). The marine concentrations have been somewhat lower, ranging from $1.0 \times 10^{10} \text{ cm}^{-3}$ to $4.0 \times 10^{10} \text{ cm}^{-3}$ (Bonsang *et al.*, 1991), whereas in Arctic the mean concentration equal to $7.8 \times 10^{10} \text{ cm}^{-3}$ has been obtained (Rasmussen *et al.*, 1983). In the present work we consider the concentration of $6.0 \times 10^{10} \text{ cm}^{-3}$ to be normal.

C_3H_3 . There is no data available about the concentrations of C_3H_3 . Therefore, we proceed from the fact, that, compared to the known concentrations of stable molecules (CH_4 , C_2H_6), the known concentrations of many radicals (CH_3 , C_2H_5) are less abundant. Since C_3H_3 is also a radical, we have evaluated C_3H_3 to be 1000 times less abundant as compared with the abundance of C_3H_4 . Thus, in the present work the concentration of $1.0 \times 10^6 \text{ cm}^{-3}$ is considered normal; the note "estimated" has been added because of the shortage of data.

C_3H_4 . The results of measurements obtained over the Atlantic Ocean have shown the concentrations of C_3H_4 to behave somewhat similarly to the concentrations of acetylene. The both concentrations were nearly equal, and the shapes of dependences of concentrations on geographical latitude were also similar (Arlander *et al.*, 1990). Additionally, the results obtained during 2 months in Sweden are also available: the concentrations of C_3H_4 have ranged between zero and $1.6 \times 10^9 \text{ cm}^{-3}$ (Mowrer and Lindskog, 1991). In the present work we consider the concentration of $1.0 \times 10^9 \text{ cm}^{-3}$ normal.

C_3H_5 . We assume that the behaviour of radical C_3H_5 and that of radical C_2H_5 are alike. The study of C_2H_5 has shown, that its concentrations should be much lower as compared with the concentrations of C_2H_6 . Now we presume the concentrations of C_3H_5 to be much smaller if compared to the concentrations of C_3H_6 . Hence, in the present work we consider the concentration of $1.1 \times 10^3 \text{ cm}^{-3}$ to be normal; the note "estimated" has been added due to the shortage of data.

C_3H_6 . It looks as if propene tends to be less abundant in the rural regions, and more abundant in the urban regions. The measurements performed in Arctic resulted in concentrations ranging from $5 \times 10^8 \text{ cm}^{-3}$ to $9.5 \times 10^9 \text{ cm}^{-3}$ (Hov *et al.*, 1989), the observed marine concentrations were between $8 \times 10^9 \text{ cm}^{-3}$ and $9.0 \times 10^{10} \text{ cm}^{-3}$ (Bonsang *et al.*, 1991), the concentrations observed in England have ranged between $1.0 \times 10^{11} \text{ cm}^{-3}$ and $3.0 \times 10^{11} \text{ cm}^{-3}$ (Colbeck and Harrison, 1985), in Austria the concentrations from $5.0 \times 10^9 \text{ cm}^{-3}$ to $3.2 \times 10^{10} \text{ cm}^{-3}$ have been found out (Puxbaum *et al.*, 1988), whereas in the city the concentrations can reach a value of about $8.6 \times 10^{11} \text{ cm}^{-3}$ (Grosjean and Kochy, 1984). In the present work we consider the concentration of $3.0 \times 10^{10} \text{ cm}^{-3}$ normal.

C₃H₇. There is no data available about the concentrations of radical C₃H₇. Therefore, we assume the concentrations of the radical C₃H₇ to be nearly equal to the concentrations of radical C₃H₅. Hence, in the current work we consider the concentration of $1.1 \times 10^3 \text{ cm}^{-3}$ normal; the note "estimated" has been added due to the shortage of data.

C₃H₈. It looks as if the concentrations of propane tend to be lower in the rural regions, and higher in the urban regions. The results of measurements performed in Arctic have shown concentrations ranging from $2.3 \times 10^9 \text{ cm}^{-3}$ to $9.0 \times 10^{10} \text{ cm}^{-3}$ (Hov *et al.*, 1984; Hov *et al.*, 1989), the marine concentrations of propane have been between $8.1 \times 10^8 \text{ cm}^{-3}$ and $4.0 \times 10^{10} \text{ cm}^{-3}$ (Bonsang *et al.*, 1991; Rudolph *et al.*, 1984b), the results obtained in England have shown the mean concentration equal to $3.0 \times 10^{11} \text{ cm}^{-3}$ (Colbeck and Harrison, 1985), whereas in Los Angeles the observed mean concentration was $2.7 \times 10^{12} \text{ cm}^{-3}$ (Grosjean and Kochy, 1984). In the present work we regard the concentration of $1.0 \times 10^{11} \text{ cm}^{-3}$ as normal.

C₄H₆. The concentrations of butadiene obtained during 2 months in Sweden were in the range from zero to $2.2 \times 10^9 \text{ cm}^{-3}$ (Mowrer and Lindskog, 1991). The result close to the ones mentioned last has been also found out in the paper (Kelly *et al.*, 1994), where, by means of the study of known results about the concentrations, the mean concentration equal to $3.5 \times 10^9 \text{ cm}^{-3}$ has been obtained. In the present work the concentration of $3.0 \times 10^9 \text{ cm}^{-3}$ is considered normal.

C₄H₇. There is no data available about the concentrations of C₄H₇. Therefore, we proceed from the fact, that the known concentrations of many radicals (CH₃, C₂H₅) are about 1000 times less abundant as compared with the known concentrations of respective stable molecules (CH₄, C₂H₆). Since C₄H₇ is also a radical, we have evaluated C₄H₇ to be 1000 times less abundant while compared to the known abundance of C₄H₈. Thus, in the present work we consider the concentration of $5.5 \times 10^7 \text{ cm}^{-3}$ to be normal; the note "estimated" has been added because of the shortage of data.

C₄H₈. The natural concentrations of butene have been measured to be between zero and $5.0 \times 10^{10} \text{ cm}^{-3}$, the urban concentrations have ranged from $2.5 \times 10^{10} \text{ cm}^{-3}$ to $5.0 \times 10^{11} \text{ cm}^{-3}$. On the whole, the urban concentrations of butene exceed the rural concentrations of it, yet that rule is not valid for all isomers of butene (Colbeck and Harrison, 1985). Besides, the arctic concentrations of butene have not exceeded a value of $1.4 \times 10^{10} \text{ cm}^{-3}$ (Hov *et al.*, 1989). In the current work we consider the concentration $5.0 \times 10^{10} \text{ cm}^{-3}$ normal.

C₄H₉. There is no data available about the concentrations of radical C₄H₉. To get an estimate, we follow the method used in case of C₄H₇. Now we proceed from the known abundance of C₄H₁₀. Thus, the concentration of $2.2 \times 10^8 \text{ cm}^{-3}$ becomes acknowledged normal; the note "estimated" has been added due to the shortage of data.

C₄H₁₀. The results of the measurements of the natural concentration of butane have shown the mean concentration equal to $3.0 \times 10^{10} \text{ cm}^{-3}$, the urban concentrations have ranged between $4.5 \times 10^{11} \text{ cm}^{-3}$ and $1.1 \times 10^{12} \text{ cm}^{-3}$ (Colbeck and Harrison, 1985), the results obtained in India have shown concentrations ranging from $5 \times 10^{10} \text{ cm}^{-3}$ to $9.5 \times 10^{11} \text{ cm}^{-3}$ (Mohand Rao and Pandit, 1988). It seems as if the arctic concentrations of butene are somewhat smaller: measurements have shown concentrations ranging between $6.8 \times 10^9 \text{ cm}^{-3}$ and

$4 \times 10^{10} \text{ cm}^{-3}$ (Hov *et al.*, 1989). In the present work we consider the concentration of $2.0 \times 10^{11} \text{ cm}^{-3}$ to be normal.

C₅H₆. There is no data available about the concentrations of radical C₅H₆. To get an estimate, we follow the method used in case of C₄H₇. Thus, we have assumed C₅H₆ to be 1000 times less abundant as compared with the known abundance of pentene. There are at least two different sets of data available about the concentrations of pentene. In conformity with the paper (Mowrer and Lindskog, 1991), the mean concentration of pentene should equal $3 \times 10^8 \text{ cm}^{-3}$, whereas the concentrations of pentene should be nearly 20 times lower as compared with the concentrations of pentane. On the other hand, results of the paper (Colbeck and Harrison, 1985) have shown the concentrations of both pentene and pentane to be nearly equal, the mean concentrations of both reached the value of $2 \times 10^{11} \text{ cm}^{-3}$. Consequently, we have to evaluate the concentration of pentene at first. We take it to be equal to $1 \times 10^9 \text{ cm}^{-3}$. After that we can complete the estimate of the concentration of C₅H₆. Thus, in the present work we regard the concentration of $1.1 \times 10^6 \text{ cm}^{-3}$ as normal; the note "estimated" has been added due to the shortage of data.

C₆H₆. The results of measurements of concentrations of benzene obtained in Arctic have shown the mean concentration equal to $8.6 \times 10^9 \text{ cm}^{-3}$ (Rasmussen *et al.*, 1983), in USA urban concentrations ranging between $3 \times 10^{10} \text{ cm}^{-3}$ and $4.6 \times 10^{11} \text{ cm}^{-3}$ have been observed (Singh *et al.*, 1985), whereas in Los Angeles air concentrations up to $1.8 \times 10^{12} \text{ cm}^{-3}$ have been found out (Grosjean and Kochy, 1984). Here, the concentration of $8.0 \times 10^{10} \text{ cm}^{-3}$ is considered normal.

C₆H₅CH₃. The mean arctic concentration of toluene has been stated to be $1.8 \times 10^9 \text{ cm}^{-3}$ (Rasmussen *et al.*, 1983), the marine concentrations obtained over the Atlantic Ocean have ranged between $8.1 \times 10^8 \text{ cm}^{-3}$ and $7 \times 10^9 \text{ cm}^{-3}$ (Rudolph *et al.*, 1984b). It looks as if the urban concentrations of toluene are somewhat higher: the urban concentrations obtained in USA have ranged from $3 \times 10^{10} \text{ cm}^{-3}$ to $2.5 \times 10^{11} \text{ cm}^{-3}$ (Singh *et al.*, 1985), whereas in Los Angeles the concentrations up to $7.8 \times 10^{11} \text{ cm}^{-3}$ have been observed (Grosjean and Kochy, 1984). In the present work we consider the concentration $2.0 \times 10^{11} \text{ cm}^{-3}$ to be normal.

3.4. Hydrocarbons containing O-, S-, N- groups

HCO. The steady-state concentration of HCO-radical can be estimated by means of known data about the chemical reactions. The main source of HCO should be the reaction $\text{OH} + \text{HCHO} \rightarrow \text{HCO} + \text{H}_2\text{O}$, the main sink should be the reaction $\text{O}_2 + \text{HCO} \rightarrow \text{CO} + \text{HO}_2$, the respective rate constants should be equal to $1.0 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ and $3.5 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ (Donahue and Prinn, 1990). Considering both the last mentioned rate constants, and the known concentrations of HCHO and O₂, the steady-state concentrations of HCO should not exceed a value of about 10 molecules per cubic centimetre. Nevertheless, it does not appear to be reasonable to consider HCO less abundant as compared with abundance of atomic hydrogen. Hence, in the present work we consider the concentration of $1.1 \times 10^3 \text{ cm}^{-3}$ to be normal; the note "estimated" has been added due to the shortage of data.

HCHO. Formaldehyde tends to be more abundant in the urban areas, and less abundant in the remote regions. The results of measurements obtained in the towns of Brazil have shown concentrations ranging from $6.2 \times 10^{10} \text{ cm}^{-3}$ to

$9.2 \times 10^{11} \text{ cm}^{-3}$ (Grosjean and Kochy, 1990), whereas in Los Angeles the concentrations between $1.1 \times 10^{11} \text{ cm}^{-3}$ and $2.3 \times 10^{12} \text{ cm}^{-3}$ have been stated (Grosjean and Kochy, 1984). At the same time the measurements performed in a semirural area in Austria have shown the concentrations ranging from $1.1 \times 10^{11} \text{ cm}^{-3}$ to $1.8 \times 10^{11} \text{ cm}^{-3}$ (Puxbaum *et al.*, 1988). During a photochemically active period the observed concentrations have been found to be more high; the marine mean concentrations have been $5.4 \times 10^9 \text{ cm}^{-3}$ (Lowe and Schmidt, 1983) or $1.1 \times 10^{10} \text{ cm}^{-3}$ (Zafiriou *et al.*, 1980). In the present work we consider the concentration of $2.0 \times 10^{11} \text{ cm}^{-3}$ normal.

CH₂S. There is no data available about the concentrations of CH₂S. To get an estimate, we proceed from the estimated concentration of CH₃S, but taking into the consideration the fact, that CH₂S is not a radical, differently from CH₃S. We know, that the concentrations of many radicals (CH₃, C₂H₅) are less abundant compared to the known concentrations of stabile molecules (CH₄, C₂H₆). Vice versa, we can assume CH₂S to be somewhat more abundant as compared with the abundance of CH₃S. Thus, in the present work we regard the concentration of $2.2 \times 10^7 \text{ cm}^{-3}$ as normal; the note "estimated" has been added because of the lack of data, now the note "estimated" is to be considered specially "strong" as the used concentration of CH₃S has already been estimated.

CH₃N. There is no data available about the concentrations of CH₃N. To get an estimate still, we proceed from the estimated concentrations of CH₃S and CH₃O, but taking into the consideration the fact that, unlike both CH₃S and CH₃O, CH₃N is not a radical. Therefore, we assume CH₃N to be somewhat more abundant as compared with the abundance of CH₃O. Hence, in the present work we consider the concentration of $2.2 \times 10^6 \text{ cm}^{-3}$ normal; the note "estimated" has been added due to the shortage of data, now the note "estimated" is to be considered specially "strong" as the used concentration of CH₃O has already been estimated.

CH₃NH. There is no data available about the concentrations of CH₃NH. For that reason we proceed from the known concentrations of methylamine. Unlike methylamine, CH₃NH has not been observed in the air. Additionally, CH₃NH appears to be a radical. Because of the facts mentioned above the concentrations of CH₃NH should be lower as compared with the concentrations of methylamine. Hence, in the present work we consider the concentration of $1.1 \times 10^6 \text{ cm}^{-3}$ to be normal; the note "estimated" has been added due to the shortage of data.

CH₃NH₂. Methylamine has been observed in the air of the Hawaiian Islands, the observed concentrations ranged between $4 \times 10^6 \text{ cm}^{-3}$ and $1 \times 10^7 \text{ cm}^{-3}$ (Van Neste *et al.*, 1987). The possible sources and sinks of methylamine have also been discussed, it seems as if methylamine originates from ocean and the main sinks of it are the reactions with OH (Van Neste *et al.*, 1987). In the current work we regard the concentration of $7 \times 10^6 \text{ cm}^{-3}$ as normal.

CH₃NO₂. As to CH₃NO₂, then only the concentrations considered as limits for field of labour protection are available, those being equal to $2.7 \times 10^{15} \text{ cm}^{-3}$ (Leite, 1980). Nevertheless, there is no reason to presume CH₃NO₂ to be actually more abundant as compared with the abundance of acetonitrile, for instance. There are some results about the concentrations of acetonitrile, but no results about the concentrations of CH₃NO₂, owing to what the actual abundance of CH₃NO₂

should not exceed the abundance of acetonitrile. Hence, in the present work we consider the concentration of $1.1 \times 10^9 \text{ cm}^{-3}$ to be normal; the note "estimated" has been added due to the shortage of data.

CH₃O. The steady-state concentration of CH₃O-radical can be estimated by means of known data about the chemical reactions. CH₃O should arise mainly by means of the reactions $\text{OH} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}_2\text{O}$, $\text{O}_2 + \text{CH}_3 \rightarrow \text{CH}_3\text{O}_2$ and $\text{NO} + \text{CH}_3\text{O}_2 \rightarrow \text{CH}_3\text{O} + \text{NO}_2$, whereas CH₃O should disappear mainly by means of the reaction $\text{O}_2 + \text{CH}_3\text{O} \rightarrow \text{CH}_2\text{O} + \text{HO}_2$ (Donahue and Prinn, 1990). To get an estimate, we make comparisons between the rates of reactions $\text{OH} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}_2\text{O}$ and $\text{O}_2 + \text{CH}_3\text{O} \rightarrow \text{CH}_2\text{O} + \text{HO}_2$. The rate constant of the first reaction is equal to $2.4 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, the rate constant of the second reaction is $3.9 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$. In accordance with the known concentrations of OH, CH₄ and O₂, the steady-state concentration of CH₃O should be about 1000 molecules per cubic centimetre. Additionally, we consider the fact that there are some supplementary reactions which can also be considered as sources of CH₃O. Thus, in the present work we consider the concentration of $2.2 \times 10^4 \text{ cm}^{-3}$ normal; the note "estimated" has been added because of the lack of data.

CH₃OH. About the methanol only the concentrations considered to be the limits for field of labour protection are available, equal to $5.4 \times 10^{15} \text{ cm}^{-3}$ (Leite, 1980). To get an estimate, we proceed from the evaluated concentration of CH₃NO₂. Thus, we assume methanol to be about two times more abundant as compared with that of CH₃NO₂, resulting in the concentration equal to $2.2 \times 10^9 \text{ cm}^{-3}$. We consider that concentration normal in the present work; the note "estimated" has been added because of the shortage of data.

It is to be noted that the actual concentration of methanol has a substantial effect on the evolution of positive ions, consequently the potential inaccuracy in the actual concentration of methanol will have a significant effect on the authenticity of the model.

CH₃S. There is no direct data available about the concentrations of CH₃S. Nevertheless, CH₃S seems to be the intermediate product of CH₃SH (Atkinson *et al.*, 1989a; Atkinson *et al.*, 1989b; Baulch *et al.*, 1980), owing to this the concentrations of CH₃S should be connected with the concentrations of CH₃SH. As CH₃S is a radical, the concentrations of it can be assumed to be lower than the concentrations of CH₃SH are. Thus, in the present work we regard the concentration of $2.2 \times 10^5 \text{ cm}^{-3}$ as normal; the note "estimated" has been added due to the shortage of data.

CH₃SH. The steady-state concentrations of CH₃SH can be estimated by means of known data about the chemical reactions. In conformity with the works (Atkinson *et al.*, 1989a; Atkinson *et al.*, 1989b; Baulch *et al.*, 1980), the reaction $(\text{CH}_3)_2\text{S} + \text{O} \rightarrow \text{CH}_3\text{O} + \text{CH}_3\text{S}$ generates CH₃S radicals. Next, the radicals CH₃S can be assumed to produce quickly CH₃SH molecules. On the other hand, CH₃SH molecules take part in the reactions $\text{CH}_3\text{SH} + \text{OH} \rightarrow \text{products}$ and $\text{CH}_3\text{SH} + \text{NO}_3 \rightarrow \text{products}$, which can be considered to be the sinks of CH₃SH; the rate constants of the reactions mentioned above are equal to $1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, $3.3 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$, and $9.2 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$. In accordance with the concentrations of OH, O, NO₃ and (CH₃)₂S stated to be normal, the steady-state concentration of CH₃SH should be about $2 \times 10^6 \text{ cm}^{-3}$. This concentration of CH₃SH can be

considered normal in the present work; the note "estimated" has been added because of the shortage of data.

CH₃SO₃H. According to the paper (Tanner and Eisele, 1991), methane sulfonic acid has a substantial effect on the evolution of negative ions. The concentrations of methane sulfonic acid have been estimated by means of observed composition of ions and supposable rates of ion-molecule reactions, consideration of which has resulted in the concentration of about $5 \times 10^6 \text{ cm}^{-3}$ (Tanner and Eisele, 1991). As no data about the ion-molecule reactions capturing molecules of methane sulfonic acid can be found, methane sulfonic acid has not been included into the present work.

CH₃CN. The near-ground concentrations of acetonitrile have been observed to be between $5.4 \times 10^{10} \text{ cm}^{-3}$ and $2.0 \times 10^{11} \text{ cm}^{-3}$ (Becker and Ionescu, 1982). On the other hand, some other works have considered acetonitrile to be less abundant. The discussions presented in paper (Brasseur *et al.*, 1985) have been proceeded from the concentration equal to $5.4 \times 10^9 \text{ cm}^{-3}$, the shape of dependence of concentrations of acetonitrile on altitude reported in the paper (Beig and Chakrabarty, 1987) results in the near-ground concentrations of about $2.7 \times 10^8 \text{ cm}^{-3}$. In the paper (Arijs, 1992) a survey of results of data about the concentrations of acetonitrile has been presented, in accordance with that survey concentrations of acetonitrile should range from $5.0 \times 10^8 \text{ cm}^{-3}$ to $3.0 \times 10^9 \text{ cm}^{-3}$.

In the present work we regard the concentration of $1.1 \times 10^9 \text{ cm}^{-3}$ as normal. Nevertheless, it seems as if the actual concentration of acetonitrile is not well known. On the other hand, evolution of positive ions depends much on the actual concentration of acetonitrile. For that reason it is to be pointed out, that the potential inaccuracy in the actual concentration of acetonitrile will have a significant effect on the authenticity of the model.

CH₃CHO. The concentrations of acetaldehyde do not show any essential dependence on the amount of pollution: the results obtained in towns of Brazil have shown concentrations ranging between $2.4 \times 10^{10} \text{ cm}^{-3}$ and $9.5 \times 10^{11} \text{ cm}^{-3}$ (Grosjean and Kochy, 1990), in Los Angeles air the concentrations ranging from $5.4 \times 10^{10} \text{ cm}^{-3}$ to $1.1 \times 10^{12} \text{ cm}^{-3}$ have been observed (Grosjean and Kochy, 1984), the results obtained in a rural area in Austria have shown concentrations between $5.0 \times 10^{10} \text{ cm}^{-3}$ and $3.7 \times 10^{11} \text{ cm}^{-3}$ (Puxbaum *et al.*, 1988). In the present work we consider the concentration of $1.5 \times 10^{11} \text{ cm}^{-3}$ to be normal.

CH₃COOH. The concentrations of acetic acid observed in a rural area in Austria have ranged from $8.0 \times 10^9 \text{ cm}^{-3}$ to $2.2 \times 10^{10} \text{ cm}^{-3}$ (Puxbaum *et al.*, 1988), the marine concentrations of CH₃COOH have been between $1.4 \times 10^9 \text{ cm}^{-3}$ and $1.7 \times 10^{11} \text{ cm}^{-3}$ (Arlander *et al.*, 1990). In the present work we regard the concentration of $1.8 \times 10^{10} \text{ cm}^{-3}$ as normal.

C₂H₂O. We assume, that a certain analogy between the formation of C₂H₅O and the formation of C₂H₂O exists. As we can see it from the discussion of formation of C₂H₅O, the abundance of C₂H₂O should be many times lower as compared with the abundance of C₂H₅. And so, the assumption about a analogy between C₂H₅O and C₂H₂O results in the abundance of C₂H₂O to be many times lower than the abundance of C₂H₂. Hence, in the present work we consider the concentration of $1.1 \times 10^6 \text{ cm}^{-3}$ to be normal; the note "estimated" has been added because of the lack of data.

C₂H₅NH. There is no data available about the concentrations of C₂H₅NH. As C₂H₅NH is a radical, the concentrations of it can be assumed to be somewhat lower than the concentrations of C₂H₅NH₂. Thus, in the present work we consider the concentration of $2.2 \times 10^5 \text{ cm}^{-3}$ normal; the note "estimated" has been added by reason of the lack of data.

C₂H₅NH₂. There is no data available about the concentrations of ethylamine, owing to that we assume the abundance of ethylamine to be nearly equal to the known abundance of methylamine. Hence, in the present work we regard the concentration of $7 \times 10^6 \text{ cm}^{-3}$ as normal; the note "estimated" has been added due to the shortage of data.

C₂H₅O. The main sources of the radical C₂H₅O should be the reactions C₂H₅+O₂ → C₂H₅O₂ and C₂H₅O₂+NO → C₂H₅O+NO₂, the main sink should be the reaction C₂H₅O+O₂ → CH₃CHO+HO₂ (Lightman *et al.*, 1990; Donahue and Prinn, 1990). Consequently, a certain analogy can be drawn between the reactions forming the concentration of C₂H₅O and the reactions forming the concentration of CH₃O but the concentration of C₂H₅ is lower as compared with the concentration of CH₃. According to the conditions mentioned above, the reactions generating C₂H₅O are slower than the reactions generating CH₃O, which results in the concentrations of C₂H₅O being lower than the concentrations of CH₃O. Hence, in the present work we consider the concentration of $1.1 \times 10^3 \text{ cm}^{-3}$ to be normal; the note "estimated" has been added by reason of the lack of data.

C₂H₅OH. There is no data available about the concentrations of ethanol. Therefore, we assume the abundance of ethanol to be nearly equal to the abundance of methanol. Thus, in the present work we consider the concentration of $2.2 \times 10^9 \text{ cm}^{-3}$ normal; the note "estimated" has been added due to the shortage of data.

(CH₃)₂NH. The concentrations of methylamine have been measured in Hawaii, the observed concentrations ranged between $3.6 \times 10^7 \text{ cm}^{-3}$ and $1.2 \times 10^8 \text{ cm}^{-3}$ (Van Neste *et al.*, 1987). In the present work we regard the concentration of $7 \times 10^7 \text{ cm}^{-3}$ as normal.

(CH₃)₂S. Dimethyl sulfide as been observed by two groups of authors: the observed concentrations have ranged from $2.0 \times 10^7 \text{ cm}^{-3}$ to $4.2 \times 10^8 \text{ cm}^{-3}$ (Barnard *et al.*, 1982), or have remained below the level of $8.0 \times 10^8 \text{ cm}^{-3}$ (Sze and Malcolm, 1980). In the current work we consider the concentration of $1.0 \times 10^8 \text{ cm}^{-3}$ normal.

(CH₃)₂SO. We assume the abundance of (CH₃)₂SO to be about 10 times less as compared with the abundance of (CH₃)₂S. This assumption can be motivated by the fact, that there are some data about the concentrations of (CH₃)₂S but no data about the concentrations of (CH₃)₂SO. Thus, in the present work we consider the concentration of $1.1 \times 10^7 \text{ cm}^{-3}$ to be normal; the note "estimated" has been added due to the shortage of data.

(CH₃)₂CO. The concentrations of acetone have been measured in the towns of Brazil, the concentrations ranged between $5.0 \times 10^9 \text{ cm}^{-3}$ and $5.5 \times 10^{11} \text{ cm}^{-3}$ (Grosjean and Kochy, 1990).

On the other hand, on the ground of some preliminary simulations realized by the author of the present work, abundance of acetone should be substantially

lower than the abundances reported above, otherwise the results obtained by virtue of the model do not match with the results obtained by means of measurements. In case we take the concentration of acetone to be equal to $5.0 \times 10^{10} \text{ cm}^{-3}$ the model results in the composition of ions where the ions containing acetone are the almost single existing ions. The results of that kind do not accord with the results of measurements of the steady-state ion composition. To get a better accordance with the results of measurements, we can decrease the concentration of acetone. In this way we obtain the new model where the "normal" concentration of acetone results in a certain composition of ions, but an increase in the concentration of acetone results in a considerable transformation in the composition of ions. Such results obtained by means of the model are in an essentially better accordance with the results of measurements. Still, they can not be regarded as the verification of decreased concentration of acetone. Anyway, in the present work we consider the decreased concentration of $5.0 \times 10^8 \text{ cm}^{-3}$ to be normal.

$\text{C}_3\text{H}_4\text{O}_4$. In conformity with the paper (Eisele, 1989a), $\text{C}_3\text{H}_4\text{O}_4$ should have an essential effect on the evolution of negative ions. On the other hand, there is no data available either about the concentrations or about the reactions capturing $\text{C}_3\text{H}_4\text{O}_4$ molecules. Therefore, we can not use $\text{C}_3\text{H}_4\text{O}_4$ in the present model.

$\text{C}_3\text{H}_5\text{O}$. There are not any results of measurements of the concentrations of $\text{C}_3\text{H}_5\text{O}$ nor any data about chemical reactions embracing molecules of $\text{C}_3\text{H}_5\text{O}$ available. Therefore quite low concentrations can be assumed. On the other hand, the absence of data about sinks indicates to the possibility of notable concentrations, which would be realized in case of presence of some unknown sources of $\text{C}_3\text{H}_5\text{O}$. For that reason we assume the concentrations of $\text{C}_3\text{H}_5\text{O}$ to be close to the concentrations of many low-abundant but stable compounds. Thus, in the present work we regard the concentration of $1.1 \times 10^8 \text{ cm}^{-3}$ as normal; the note "estimated" has been added due to the shortage of data.

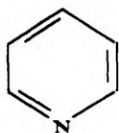
$(\text{CH}_3)_3\text{N}$. Trimethylamine has been observed in the air of the Hawaiian Islands, the observed concentrations have ranged between $6.6 \times 10^6 \text{ cm}^{-3}$ and $3 \times 10^7 \text{ cm}^{-3}$ (Van Neste *et al.*, 1987). The possible sources and sinks of trimethylamine have also been discussed, it seems as if trimethylamine originates from the ocean and the main sinks of it are the reactions with OH (Van Neste *et al.*, 1987). Thus, we could consider the concentration of $1.5 \times 10^7 \text{ cm}^{-3}$ normal but since there is no data about the respective ion-molecule reactions available, we can not use trimethylamine in the present model.

$(\text{CH}_3)_2\text{NCHO}$. Dimethyl formamide has an effect on the mobility spectrum of positive ions (see discussion in Article 2.4.5), and that is why it should be included in the model. The actual concentrations of dimethyl formamide in the air show a wide variation, being often below the detection limit but sometimes the concentrations can reach values of about $1 \times 10^{11} \text{ cm}^{-3}$ (Kelly *et al.*, 1994). Nevertheless, any data about the ion-molecule reactions embracing molecules of dimethyl formamide could not be found. In consequence of this fact we can not use dimethyl formamide in this model.

$\text{C}_3\text{H}_7\text{OH}$. We assume buthanol to be somewhat less abundant as compared with the abundance of either methanol or ethanol. Thus, in the present work we

consider the concentration of $1.1 \times 10^9 \text{ cm}^{-3}$ to be normal; the note “estimated” has been added due to the shortage of data.

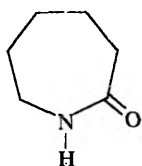
C₅H₅N. There is no data available about the concentrations of pyridine. On the one hand, the concentrations of pyridine should be somewhat connected with the concentrations of terpenes as both pyridine and terpenes come of coniferous forests. Unlike the concentrations of pyridine, the concentrations of some terpenes (pinene, limonene, camphene) have been measured, the concentrations ranged between $5 \times 10^8 \text{ cm}^{-3}$ and $1 \times 10^{11} \text{ cm}^{-3}$ (Bufler and Wegmann, 1991; Riba *et al.*, 1987; Juuti *et al.*, 1990). As to the concentrations of pyridine then, they have only been estimated by means of data about the observed composition of ions, on the one hand, and known data about the ion-molecule reactions, on the other hand; such procedure has resulted in the mean concentration equal to $6.7 \times 10^7 \text{ cm}^{-3}$ (Tanner and Eisele, 1991). The authors of the result mentioned last have considered the result as a rough estimate.



On the other hand, on the ground of some preliminary simulations, realized by the author of present work, the abundance of pyridine should be substantially less than the abundances of terpenes, otherwise the results obtained by virtue of the model would not match with the results obtained by means of measurements. In case we take the concentration of pyridine to be equal to $1 \times 10^9 \text{ cm}^{-3}$ the model results in the composition of ions where the ions containing pyridine are the almost single existing ions, that is specially in case of the increased concentrations of NH_3 . The results of this kind do not accord with the results of measurements of steady-state ion composition. To get a better accordance with the results of measurements, we can decrease the concentration of pyridine. This way we obtain the new model where the “normal” concentration of pyridine results in a certain composition of ions, but an increase in the concentration of pyridine results in a considerable transformation in the composition of ions. Such results obtained by means of the model are in essentially better accordance with the results of measurements, for all that they can not be considered to be a verification of decreased concentration of pyridine. Nevertheless, the concentrations of pyridine should be really lower than the concentrations of terpenes because of the fact, that the concentrations of terpenes have been measured whereas the concentrations of pyridine have not been. Thus, in the present work we consider the decreased concentration of $9 \times 10^6 \text{ cm}^{-3}$ to be normal; the note “estimated” has been added due to the insufficiency of data.

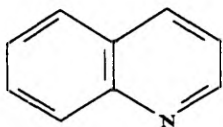
CH₃COC₃H₇. There are no results of measurements of the concentrations of CH₃COC₃H₇ nor any data about chemical reactions including molecules of CH₃COC₃H₇ available. For that reason we assume the concentrations of CH₃COC₃H₇ to be close to the concentrations of many low-abundant but stable compounds. Thus, in the present work we regard the concentration of $1.1 \times 10^8 \text{ cm}^{-3}$ as normal; the note “estimated” has been added due to the shortage of data.

(C₂H₅)₃N. We assume the abundance of triethylamine to be nearly equal to the abundance of trimethylamine. Thus, in the present work we consider the concentration of $1.5 \times 10^7 \text{ cm}^{-3}$ to be normal; the note “estimated” has been added because of the shortage of data.



C₆H₁₀ONH. In conformity with the paper (Tanner and Eisele, 1991), caprolactam has an effect on the composition of positive ions. That is why it should be included in the model. Nevertheless, any data about the ion-molecule reactions capturing molecules of caprolactam could not be found, consequently we can not use caprolactam in this model.

C₉H₉N. In conformity with the paper (Tanner and Eisele, 1991), quinoline has an effect on the composition of positive ions. That is why it should be included in the model. Nevertheless, no data about the ion-molecule reactions capturing molecules of quinoline could be found, and therefore we can not use quinoline in this paper.



3.5. Other compounds

C. There can be found no results of measurements of the concentrations of C nor any data about chemical reactions including atoms of C. Therefore, comparatively low concentrations can be assumed. We presume the abundance of C to be nearly equal to the abundance of O. Thus, in the present work we consider the concentration of $1.1 \times 10^5 \text{ cm}^{-3}$ to be normal; the note "estimated" has been added by reason of the shortage of data.

CIN. As the concentrations of CIN regard, the consideration used in the discussion about the concentrations of C can be employed here in many aspects. CIN is a stabile compound, but the stabile compounds are, as a rule, considered to be more abundant than radicals in the present work. For that reason we assume the concentrations of CIN to be only somewhat lower as compared with the concentrations which are near detection limits. Thus, in the present work we regard the concentration of $1.1 \times 10^8 \text{ cm}^{-3}$ as normal; the note "estimated" has been added due to the lack of data.

CS. There are no results of measurements available about the concentrations of CS. Therefore, we employ the known data about the chemical reactions embracing molecules of CS. In conformity with the works (Atkinson *et al.*, 1989a; Atkinson *et al.*, 1989b; Baulch *et al.*, 1980), the main source of CS should be the reaction $\text{O} + \text{CS}_2 \rightarrow \text{SO} + \text{CS}$; the main sink should be the reaction $\text{O} + \text{CS} \rightarrow \text{S} + \text{CO}$. As the rate constant of the source reaction exceeds about 10 times the rate constant of the sink reaction, the steady-state concentration of CS should be about 10 times higher than the concentration of CS₂. Moreover, a supposable scheme of reactions between CS₂, CS, COS, HS, HSO and H₂S presented in the paper (Sze and Malcolm, 1980) contains an additional source of CS, namely, the reaction $\text{OH} + \text{CS}_2 \rightarrow \text{HSO} + \text{CS}$, although the notes about both the endothermity and the absence of exact data also belong to that reaction. On the other hand, the treatment started above results in the concentrations of CS close to the concentrations of gases such as HNO₃, for instance. In that case, some results of measurements of the concentrations of CS should be available, yet, no observation is known. Thus, the concentrations of CS should not be comparable with the concentrations of HNO₃. Taking the aspects mentioned above into consideration, we additionally examine the paper (Schofield, 1973), according to which, the abundance of CS should exceed the abundance of CS₂ as

all the reactions decreasing the concentrations of CS appear to be quite slow, still, the rate constant of the reaction $O+CS_2 \rightarrow SO+CS$ exceeds the rate constant of the reaction $O+CS \rightarrow S+CO$ as before. As a summary, in the present work we consider the concentration of $1.1 \times 10^9 \text{ cm}^{-3}$ to be normal; the note "estimated" has been added because of the shortage of data.

CS₂. The photochemical model used in the paper (Sze and Malcolm, 1980) has resulted in the concentration of carbon disulfide ranging between the values of $1.9 \times 10^9 \text{ cm}^{-3}$ and $1.0 \times 10^{10} \text{ cm}^{-3}$. Besides, the paper (Kelly *et al.*, 1994) has presented a survey of results of known observations resulting in the mean value of the concentration equal to $7.5 \times 10^8 \text{ cm}^{-3}$. In the present work we regard the concentration of $7.5 \times 10^8 \text{ cm}^{-3}$ as normal.

C₂N₂. As to C₂N₂, only the concentrations considered the limits for the field of labour protection are available, equal to $2.7 \times 10^{14} \text{ cm}^{-3}$ (Leite, 1980). As the concentration mentioned last is equal to the concentration of methylamine obtained from the work (Leite, 1980), and there is no reason to assume the concentrations of C₂N₂ to be essentially different from the concentrations of methylamine, in the present work the concentration of $7 \times 10^6 \text{ cm}^{-3}$ is considered normal, whereas the note "estimated" has been added due to the shortage of data.

C₂O. There are neither any results of measurements of the concentrations of C₂O nor any data about the chemical reactions including molecules of C₂O available. Therefore, quite low concentrations can be assumed. On the other hand, C₂O is a stabile compound, and the stabile compounds are, as a rule, considered to be quite abundant in the present work. For that reason, we assume the concentrations of C₂O to be close to the known concentrations which are near the detection limits. Thus, in the present work we consider the concentration of $1.1 \times 10^8 \text{ cm}^{-3}$ normal; the note "estimated" has been added due to the lack of data.

H. There are no results of measurements of the concentrations of H, but a lot of data about the chemical reactions including atoms of H. Nevertheless, it appears to be quite useless to construct a scheme of reactions as the scheme of that kind would be unclear because of a large number of the processes including atoms of H. As a result of the complexity of such scheme, we probably can not obtain the value of steady-state concentration of H. Thus, we proceed from the estimate equal to $1.3 \times 10^4 \text{ cm}^{-3}$ reported in paper (Lifshitz *et al.*, 1984), and from the information about the near-ground concentrations of O being below the value of $1 \times 10^6 \text{ cm}^{-3}$ according to the paper (Turco *et al.*, 1979). As the authors of the paper (Lifshitz *et al.*, 1984) have evaluated the concentrations of O to be about $1.3 \times 10^8 \text{ cm}^{-3}$, it could be assumed that all the values of concentrations of N, O and H reported in the paper (Lifshitz *et al.*, 1984) were actually exaggerated. Taking all this into account, we consider the actual concentrations of H to be 10 times lower than the concentrations reported by the paper (Lifshitz *et al.*, 1984). Hence, in the present work we consider the concentration of $1.1 \times 10^3 \text{ cm}^{-3}$ to be normal; the note "estimated" has been added by reason of the lack of data.

HN. There can be found neither any results of measurements of the concentrations of HN nor any data about the chemical reactions involving the molecules of HN. Therefore, quite low concentrations can be assumed. Besides, HN is a radical, but radicals are, as a rule, considered to be less abundant as compared to the abundance of any stabile compound in the present work. For

that reason, we assume the concentrations of HN to be close to the concentrations of N, for instance. Thus, in the present work we regard the concentration of $1.1 \times 10^4 \text{ cm}^{-3}$ as normal; the note "estimated" has been added because of the shortage of data.

HNO. There are neither any results of measurements of the concentrations of HNO nor any data about the chemical reactions with the molecules of HNO available. Therefore, quite low concentrations can be assumed. Still, HNO is a stabile compound, but the stabile compounds are in the present work, as a rule, considered to be notably abundant, at least more abundant than the concentrations of radicals such as H, N, or CH. For that reason we assume the concentrations of HNO to be close to the concentrations near detection limits. Thus, in the present work we consider the concentration of $1.1 \times 10^7 \text{ cm}^{-3}$ to be normal; the note "estimated" has been added due to the shortage of data.

HNO₂. The concentrations of nitrous acid have been measured in a city during a 5 month period, the observed concentrations have ranged between the values from $6 \times 10^8 \text{ cm}^{-3}$ to $3 \times 10^{10} \text{ cm}^{-3}$ (Sjödín and Ferm, 1985). In the present work we consider the concentration of $1.5 \times 10^9 \text{ cm}^{-3}$ normal.

HN₂O. There can be found no results of measurements of the concentrations of HN₂O nor any data about the chemical reactions embracing the molecules of HN₂O. Therefore, quite low concentrations can be presumed. Besides, HN₂O is a radical, but radicals are, as a rule, considered to be less abundant than any other stabile compound in the present work, as the known concentrations of many radicals (CH₃, C₂H₅) are less abundant as compared with the known concentrations of stabile molecules (CH₄, C₂H₆). Thus, in the present work we regard the concentration of $1.1 \times 10^4 \text{ cm}^{-3}$ as normal; the note "estimated" has been added because of the shortage of data.

HO₂. The near-ground concentrations of HO₂ can be estimated by virtue of known shape of dependence of concentrations of HO₂ on the altitude. According to the paper (Turco *et al.*, 1979), the respective mean concentration should be about $1 \times 10^{12} \text{ cm}^{-3}$

HO₂ molecules should arise by means of the reactions $\text{CO} + \text{OH} \rightarrow \text{H} + \text{CO}_2$ and $\text{H} + \text{O}_2 \rightarrow \text{HO}_2$, whereas the reactions $\text{NO} + \text{HO}_2 \rightarrow \text{OH} + \text{NO}_2$ and $\text{O}_3 + \text{HO}_2 \rightarrow \text{OH} + 2\text{O}_2$ can be considered to be the sinks of HO₂ (Eisele and Tanner, 1991). Additionally, according to the information reported in the paper mentioned last, the reaction $\text{CO} + \text{OH} \rightarrow \text{H} + \text{CO}_2$ appears to be the main sink of OH. As so, the reactions presented hereinbefore partially determine the ratio between the concentrations of OH and HO₂. Unfortunately, no data about the values of the rate constants of the respective reactions can be found. Therefore, we assume the values of all rate constants to be nearly equal; the equilibrium of a reaction is determined by the concentrations of substances participating in the reaction. Since the concentration of CO is roughly equal to the concentrations of both NO and O₃, the concentrations of OH and HO₂ should also be almost equal. Nevertheless, some additional reactions essential to the concentrations of HO₂ have been reported in the papers (Donahue and Prinn, 1990; Hough, 1991). Thus, we can not make the decision about the concentrations of HO₂ only by means of the reactions presented above.

Next we scan the paper (Donahue and Prinn, 1990) where the concentration of HO_2 is considered to be 100 times higher than the concentration of OH. Since we have no objection against the last mentioned value of the concentration of HO_2 , in the present work we consider the concentration of $1.5 \times 10^8 \text{ cm}^{-3}$ normal.

HS. To obtain an estimate to the steady-state concentration of HS we employ the known data about the chemical reactions with HS. The sources of HS should be the reactions $\text{OH} + \text{H}_2\text{S} \rightarrow \text{HS} + \text{H}_2\text{O}$ and $\text{O} + \text{H}_2\text{S} \rightarrow \text{HS} + \text{OH}$, whereas sinks should be the reactions $\text{HS} + \text{O}_3 \rightarrow \text{HSO} + \text{O}_2$, $\text{HS} + \text{NO}_2 \rightarrow \text{products}$, and $\text{HS} + \text{NO} + \text{N}_2 \rightarrow \text{products}$. In conformity with the data reported in the works (Atkinson *et al.*, 1989a; Atkinson *et al.*, 1989b; Baulch *et al.*, 1980), the values of the respective rate constants are $4.8 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, $2.2 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$, $3.6 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, $5.8 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$, and $2.4 \times 10^{-31} \text{ cm}^6 \text{ s}^{-1}$. By virtue of the reported values of rate constants, on the one hand, and of the known concentrations of H_2S , O, OH, NO, NO_2 and O_3 , on the other hand, we obtain the steady-state concentration of $1.1 \times 10^6 \text{ cm}^{-3}$ considered normal in the present work; the note "estimated" has been added by reason of the shortage of data.

H_2O_2 . The concentrations of H_2O_2 evaluated by means of a photochemical model range between $8.6 \times 10^{10} \text{ cm}^{-3}$ and $1.4 \times 10^{11} \text{ cm}^{-3}$ (Kleinman, 1986). Besides, the results of the observations obtained both in Dortmund and Brazil have shown concentrations ranging from $3 \times 10^8 \text{ cm}^{-3}$ to $1.1 \times 10^{11} \text{ cm}^{-3}$ (Jacob *et al.*, 1990), whereas the results obtained in USA have shown concentrations between $5.4 \times 10^9 \text{ cm}^{-3}$ and $1.1 \times 10^{11} \text{ cm}^{-3}$ (Heikes *et al.*, 1987; Hough, 1991). The concentrations of H_2O_2 appear to be slightly dependent on the altitude; the near-ground concentrations are about 2 times higher than the concentrations at a level of about 3 km. Nevertheless, often no considerable dependence on the altitude can be observed (Heikes *et al.*, 1987). In the present work we consider the concentration of $1.0 \times 10^{10} \text{ cm}^{-3}$ to be normal.

H_3O . The concentration of the radical H_3O is considered to be nearly equal to the concentrations of the radical OH, hence, in the present work we regard the concentration of $2.0 \times 10^6 \text{ cm}^{-3}$ as normal; the note "estimated" has been added due to the shortage of data.

N. As regards the concentration of N, the situation here appears to be somewhat similar to the that concerning the estimate of the concentration of H. Here the estimate presented in the paper (Lifshitz *et al.*, 1984) is equal to $1.3 \times 10^6 \text{ cm}^{-3}$, and the information about the near-ground concentrations of O is the same as the one in case of H. Hence, in the present work we consider the concentration of $1.1 \times 10^4 \text{ cm}^{-3}$ normal; the note "estimated" has been added by reason of the lack of data.

NH_2 . We proceed from the fact, that the known concentrations of many radicals (CH_3 , C_2H_5) are much less abundant as compared with the known concentrations of stable molecules (CH_4 , C_2H_6). Since NH_2 is also a radical, we evaluate the concentration of NH_2 being 1000 times lower than that of NH_3 . Therefore, in the present work we regard the concentration of $1.1 \times 10^7 \text{ cm}^{-3}$ as normal; the note "estimated" has been added because of the lack of data.

NO_3 . According to the classic work (Junge, 1965), the total concentration of NO, NO_3 and N_2O_5 should be about some per cent of the concentration of NO_2 .

The results obtained by virtue of the model calculations have shown the mean concentration equal to $3.9 \times 10^7 \text{ cm}^{-3}$ (Donahue and Prinn, 1990).

On the other hand, the observations in mountains have resulted in the mean concentration equal to $5 \times 10^9 \text{ cm}^{-3}$, whereas the urban concentration of NO_3 should be lower because of many additional chemical reactions considered additional sinks of NO_3 (Noxon *et al.*, 1980). In conformity with the paper (Platt *et al.*, 1984), the results obtained in the near-ground air appear to be quite different: sometimes the concentrations did not exceed the detection limit equal to $2 \times 10^7 \text{ cm}^{-3}$, whereas the concentration of about $5 \times 10^9 \text{ cm}^{-3}$ has also been observed. The higher concentrations can be observed only at night as light causes the dissociation of NO_3 (Solomon *et al.*, 1989).

In the present work we regard the concentration of $3 \times 10^8 \text{ cm}^{-3}$ as normal. N_2O_5 . According to the classic work (Junge, 1965), the summary concentration of NO , NO_3 and N_2O_5 should be about some per cent of the concentration of NO_2 . Besides, the concentrations of N_2O_5 and NO_3 are connected by the reactions $\text{NO}_2 + \text{NO}_3 \rightarrow \text{N}_2\text{O}_5$ and $\text{N}_2\text{O}_5 \rightarrow \text{NO}_2 + \text{NO}_3$ (Platt *et al.*, 1984; Atkinson *et al.*, 1984), whereas the respective rate constants have the values of $5.7 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ and 3.3 s^{-1} (Atkinson *et al.*, 1989a). In the paper (Carney and Fishman, 1986) a reaction regarded as an additional sink of N_2O_5 has been reported: $\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3$, with the rate constant equal to $1.0 \times 10^{-20} \text{ cm}^3 \text{ s}^{-1}$; yet, the reaction mentioned last has not been confirmed by the work (Atkinson *et al.*, 1989a), that is why we can not take this reaction into account.

In conformity with the data, reported by the papers (Platt *et al.*, 1984; Atkinson *et al.*, 1984; Atkinson *et al.*, 1989a), the steady-state concentrations of NO_3 and N_2O_5 should be nearly equal. Thus, in the present work we consider the concentration of $3 \times 10^8 \text{ cm}^{-3}$ to be normal; the note "estimated" has been added because of the shortage of data.

O. As regards the concentration of O, the situation here appears to be somewhat similar to that discussed by the estimate of the concentration of H. Now the estimate reported by the paper (Lifshitz *et al.*, 1984) is equal to $1.3 \times 10^8 \text{ cm}^{-3}$, and the information about the near-ground concentration of O is the same as in case of H. Hence, in the present work we regard the concentration of $1.3 \times 10^5 \text{ cm}^{-3}$ as normal; the note "estimated" has been added by reason of the lack of data.

OH. As to the concentration of the radical OH, there can be found both the results of observations, and the results obtained by virtue of models. A sample is presented here as follows. The results obtained in Antarctic have shown concentrations ranging between $1.2 \times 10^4 \text{ cm}^{-3}$ and $3.8 \times 10^5 \text{ cm}^{-3}$ (Sheppard *et al.*, 1983), the observations in moderately populated regions have shown concentrations as follows: from $1.6 \times 10^6 \text{ cm}^{-3}$ to $2.5 \times 10^6 \text{ cm}^{-3}$ (Hübler *et al.*, 1984), between $5.0 \times 10^5 \text{ cm}^{-3}$ and $2.0 \times 10^7 \text{ cm}^{-3}$ (Karol *et al.*, 1983), from $5.0 \times 10^5 \text{ cm}^{-3}$ to $2.0 \times 10^6 \text{ cm}^{-3}$ (Eisele and Tanner, 1991). The survey of observations (Hewitt and Harrison, 1985) has shown the concentrations of OH ranging from zero to $1.5 \times 10^8 \text{ cm}^{-3}$.

The concentrations of OH show a strong diurnal variation: only the daytime concentrations considerably differ from zero. The diurnal variation is caused by the main source of OH requiring atoms of $\text{O}(^1\text{D})$, which arise by virtue of

photolyse from the ozone (Hewitt and Harrison, 1985; Eisele and Tanner, 1991, Donahue and Prinn, 1990). The main sinks of OH are the reactions with CO, NO₂ and CH₄ molecules (Hewitt and Harrison, 1985). The concentrations of OH show a wide variation as OH is one of the most chemically active compounds of the air (Mitra, 1990). The results obtained by virtue of models have shown concentrations ranging from $5 \times 10^4 \text{ cm}^{-3}$ to $5 \times 10^6 \text{ cm}^{-3}$, whereas the concentrations depend on the geographical latitude (Isaksen and Hov, 1987; Sze and Malcolm, 1980).

In the present work we consider the concentration of $1.5 \times 10^6 \text{ cm}^{-3}$ normal.

S. We proceed from the known data about the chemical reactions. So, the main sources of S should be the reactions $\text{O} + \text{CS}_2 \rightarrow \text{S} + \text{COS}$ and $\text{O} + \text{CS} \rightarrow \text{S} + \text{CO}$, the main sink should be the reaction $\text{S} + \text{O}_2 \rightarrow \text{SO} + \text{O}$ (Atkinson *et al.*, 1989a; Atkinson *et al.*, 1989b; Baulch *et al.*, 1980). In conformity with the data reported in the works mentioned last, and with the concentrations of O, CS₂ and CS regarded as normal, the steady-state concentrations of S should be near zero, because of the very low concentration of O. Thus, by means of the reactions mentioned above we can not obtain any reasonable concentration of S. Nevertheless, it appears not reasonable to assume the concentration of S equal to zero, which would result in excluding of S from the model. Therefore, we assume the concentration of S to be equal to the concentration of H. Hence, the concentration of $1.1 \times 10^3 \text{ cm}^{-3}$ becomes to be considered normal; the note "estimated" has been added by reason of the lack of data.

SiH₄. SiH₄ participates in ion-molecule reactions with the ions of C₂H₂⁺, C₂H₄⁺, CH₄⁺, CH₃⁺, and CH₂⁺. Under the normal conditions the concentrations of all the ions mentioned last are very low, that is why SiH₄ does not have any considerable effect on the evolution of ions. Nevertheless, it does not seem reasonable to exclude SiH₄ from the model, because of generalization of the model. For that reason we assume the concentrations of SiH₄ to be close to the known concentrations of stable compounds being near detection limits. Thus, in the present work we consider the concentration of $1.1 \times 10^7 \text{ cm}^{-3}$ to be normal; the note "estimated" has been added due to the shortage of data.

SO. Conformably to the paper (Schofield, 1973), SO should arise mainly by virtue of the reaction $\text{SO}_2 + \text{Ar} \rightarrow \text{SO} + \text{O} + \text{Ar}$, whereas the main sink reaction should be $\text{SO} + \text{O}_2 \rightarrow \text{SO}_2 + \text{O}$. Taking into account the reported data about the reactions, and the concentrations of SO₂ and Ar considered to be normal, we obtain the estimate for the steady-state concentration of SO equal to $1 \times 10^{11} \text{ cm}^{-3}$. For comparison, we can use knowledge about the valency of sulphur, pointing the valency equal to 2 to be energetically more useful than the valency equal to 4 (Knorre *et al.*, 1990). As the valency equal to 4 occurs in case of SO₂, the concentration of SO should not be lower than the concentration of SO₂, considered to be equal to $3 \times 10^{10} \text{ cm}^{-3}$. As we can see, the results of the both estimates are quite close. Thus, in the present work we regard the concentration of $1.1 \times 10^{11} \text{ cm}^{-3}$ as normal; the note "estimated" has been added because of the shortage of direct data.

SO₃. The main sources of SO₃ should be the reactions $\text{SO}_2 + \text{OH} \rightarrow \text{HSO}_3$ and $\text{HSO}_3 + \text{O}_2 \rightarrow \text{SO}_3 + \text{HO}_2$, whereas the main sink should be the reaction $\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$ (Eisele and Tanner, 1991). As regards the sources of SO₃,

the first reaction can be considered to be the limiting stage as the reaction $\text{HSO}_3 + \text{O}_2 \rightarrow \text{SO}_3 + \text{HO}_2$ is very fast. As to the sinks, the actual rate of the sink reaction can not be determined as only the upper limit of rate constant of the reaction is known. The slower the sink reaction is, the more abundant is SO_3 . In case the reported upper limit of rate constant does not differ much from the actual value of it, the concentration of SO_3 is about some hundred molecules per cubic centimeter. The assumption about the comparatively low abundance of SO_3 appears to be supported by the knowledge about the valency of sulphur. Namely, the valency of sulphur equal to 4 (in case of SO_2) is energetically more useful than the valency of sulphur equal to 6 (Knorre *et al.*, 1990).

We assume the rate constant of the sink reaction to be about 100 times lower than the reported upper limit. Hence, in the present work we regard the concentration of $2.2 \times 10^5 \text{ cm}^{-3}$ as normal; the note "estimated" has been added by reason of the shortage of data.

SO₄. Although SO_4 has been assumed to arise by means of oxidization of SO_2 in case of the presence of NO_2 and hydrocarbons (Rasul, 1976), there are no results of measurements of the concentrations of SO_4 nor any data about the chemical reactions with the molecules of SO_4 available. As regards the ions of SO_4 , their abundance has been observed to be roughly equal to the abundance of the molecules of SO_2 , although the ratio depends on the geographical latitude (Kuttler, 1984). In this work we assume a considerable part of the of ions SO_4^- coming directly from the of molecules SO_4 . Thus, in the present work we consider the concentration of $1.1 \times 10^{10} \text{ cm}^{-3}$ normal; the note "estimated" has been added due to the lack of data.

Table 3.2. Natural concentrations of neutral compounds.

Gas	Concentration	Gas	Concentration
Air	2.7×10^{19}	Ar	2.7×10^{17}
Kr	3.0×10^{13}	He	1.4×10^{14}
O ₂	5.6×10^{18}	N ₂	2.1×10^{19}
H ₂ O	2.7×10^{17}	CH ₄	4.0×10^{13}
CO	3.0×10^{12}	CO ₂	9.0×10^{15}
COS	1.3×10^{10}	HCN	4.3×10^9
HNO ₃	1.0×10^{10}	H ₂	1.5×10^{13}
H ₂ S	1.0×10^{10}	H ₂ SO ₄	4.0×10^6
NH ₃	1.0×10^{10}	NO	5.0×10^9
NO ₂	7.0×10^{10}	N ₂ O	8.0×10^{12}
O ₃	1.0×10^{12}	SO ₂	3.0×10^{10}
BrNO ₂	$*1.1 \times 10^9$	CF ₃	$*1.1 \times 10^6$
CF ₄	1.9×10^9	CClF ₃	$*2.2 \times 10^8$
CCl ₂	$*5.5 \times 10^7$	CCl ₂ F	$*3.3 \times 10^6$
CCl ₂ F ₂	7.5×10^9	CCl ₃	$*5.5 \times 10^6$
CCl ₃ F	5.0×10^9	CCl ₄	5.0×10^9
CHClF	$*1.1 \times 10^6$	CHClF ₂	$*1.4 \times 10^9$
CHCl ₂	$*5.5 \times 10^6$	CHCl ₂ F	3.8×10^8
CHCl ₃	5.0×10^9	CHF ₂	$*2.2 \times 10^5$
CHF ₃	$*2.2 \times 10^8$	CH ₂ Br	$*4.4 \times 10^5$
CH ₂ Cl	$*2.2 \times 10^7$	CH ₂ F	$*2.2 \times 10^5$
CH ₂ Cl ₂	2.1×10^9	CH ₂ F ₂	$*2.2 \times 10^9$
CH ₃ Br	3.9×10^8	CH ₃ Cl	2.0×10^{10}
CH ₃ F	$*2.2 \times 10^8$	C ₂ F ₄	$*1.1 \times 10^9$

Table 3.2. Natural concentrations of neutral compounds (continued).

C_2F_5	$*1.1 \times 10^5$	C_2F_6	2.0×10^8
C_2HF_3	$*3.3 \times 10^9$	$C_2H_2F_2$	$*3.3 \times 10^8$
$C_2H_2Cl_2$	$*3.3 \times 10^8$	C_2H_3Cl	$*3.3 \times 10^8$
C_2H_3F	$*3.3 \times 10^8$	C_2H_4F	$*1.1 \times 10^5$
C_2H_5Cl	1.1×10^8	C_3F_8	$*1.1 \times 10^7$
C_3H_4F	$*5.5 \times 10^4$	$C_6H_4F_2$	$*2.2 \times 10^6$
$ClNO_2$	$*1.1 \times 10^9$	ClO	$*1.1 \times 10^6$
Cl_2	$*1.2 \times 10^{10}$	Cl_2O	$*1.1 \times 10^8$
F	$*1.1 \times 10^3$	FNO_2	$*1.1 \times 10^9$
HBr	4.1×10^7	HCl	1.2×10^{10}
HF	$*4.4 \times 10^6$	SF_3	$*1.1 \times 10^6$
SF_4	$*1.1 \times 10^7$	SF_5	$*1.1 \times 10^6$
SF_6	1.0×10^7	CH	$*1.1 \times 10^3$
CH_2	$*1.1 \times 10^3$	CH_3	$*1.3 \times 10^4$
C_2H	$*1.6 \times 10^7$	C_2H_2	1.6×10^{10}
C_2H_3	$*3.0 \times 10^7$	C_2H_4	3.0×10^{10}
C_2H_5	$*1.1 \times 10^2$	C_2H_6	6.0×10^{10}
C_3H_3	$*1.0 \times 10^6$	C_3H_4	1.0×10^9
C_3H_5	$*1.1 \times 10^3$	C_3H_6	3.0×10^{10}
C_3H_7	$*1.1 \times 10^3$	C_3H_8	1.0×10^{11}
C_4H_6	3.0×10^9	C_4H_7	$*5.5 \times 10^7$
C_4H_8	5.0×10^{10}	C_4H_9	$*2.2 \times 10^8$
C_4H_{10}	2.0×10^{11}	C_5H_6	$*1.1 \times 10^6$
C_6H_6	8.0×10^{10}	$C_6H_5CH_3$	2.0×10^{11}
HCO	$*1.1 \times 10^3$	$HCHO$	2.0×10^{11}
CH_2S	$*2.2 \times 10^7$	CH_3N	$*2.2 \times 10^6$

Table 3.2. Natural concentrations of neutral compounds (continued).

CH ₃ NH	*1,1×10 ⁶	CH ₃ NH ₂	7.0×10 ⁶
CH ₃ NO ₂	*1.1×10 ⁹	CH ₃ O	*2.2×10 ⁴
CH ₃ OH	*2.2×10 ⁹	CH ₃ S	*2.2×10 ⁵
CH ₃ SH	*2.2×10 ⁶	CH ₃ CN	1.1×10 ⁹
CH ₃ CHO	1.5×10 ¹¹	CH ₃ COOH	1.8×10 ¹⁰
C ₂ H ₂ O	*1.1×10 ⁶	C ₂ H ₅ NH	*2.2×10 ⁵
C ₂ H ₅ NH ₂	*7.0×10 ⁶	C ₂ H ₅ O	*1.1×10 ³
C ₂ H ₅ OH	*2.2×10 ⁹	(CH ₃) ₂ NH	7.0×10 ⁷
(CH ₃) ₂ S	1.0×10 ⁸	(CH ₃) ₂ SO	*1.0×10 ⁷
(CH ₃) ₂ CO	5.0×10 ⁸	C ₃ H ₅ O	*1.1×10 ⁸
C ₃ H ₇ OH	*1.1×10 ⁹	C ₅ H ₅ N	*9.0×10 ⁶
CH ₃ COC ₃ H ₇	*1.1×10 ⁸	(C ₂ H ₅) ₃ N	*1.5×10 ⁷
C	*1.1×10 ⁵	CIN	*1.1×10 ⁸
CS	*1.1×10 ⁹	CS ₂	7.5×10 ⁸
C ₂ N ₂	*7.0×10 ⁶	C ₂ O	*1.1×10 ⁸
H	*1.1×10 ³	HN	*1.1×10 ⁴
HNO	*1.1×10 ⁷	HNO ₂	1.5×10 ⁹
HN ₂ O	*1.1×10 ⁴	HO ₂	1.5×10 ⁸
HS	*1.1×10 ⁶	H ₂ O ₂	1.0×10 ¹⁰
H ₃ O	*2.0×10 ⁶	N	*1.1×10 ⁴
NH ₂	*1.1×10 ⁷	NO ₃	3.0×10 ⁸
N ₂ O ₅	*3.0×10 ⁸	O	*1.3×10 ⁵
OH	1.5×10 ⁶	S	*1.1×10 ³
SiH ₄	*1.1×10 ⁷	SO	*1.1×10 ¹¹
SO ₃	*2.2×10 ⁵	SO ₄	*1,1×10 ¹⁰

In cubic centimeters. Asterisk, estimated concentration, see text for details.

4. SUMMARY OF RESULTS

As it was said above, most of the results obtained have already been published in papers by the author of the present work enumerated in the List of Original Publications, owing to which the results will not be revised in this Chapter. On the other hand, the published papers do not include any sufficiently thoroughgoing motivation of this model, that is why, the detailed motivation has been included into the present work as it was seen in the previous Chapters. As to the results, only a comparatively brief discussion is presented.

4.1. Evolution of positive ions

Some quantitative results obtained by virtue of simulation of the evolution of positive ions are presented in Tables 4.1, 4.2, and 4.3; some illustrative results are depicted in Figures 4.1 and 4.2. As it was shown in Chapter 2, it would not be rational to deal in details with concentrations of individual ion species as the available results of observations mainly contain information about (relative) summary abundances of the classes of ions. Therefore, the 207 ion species included in this model will not be enumerated one by one, instead, six conventional "ions" denoting all the ions of respective classes will be discussed: $\text{CH}_3\text{OH}^+\cdot\text{X}\cdot\text{Y}$, $\text{CH}_3\text{CN}^+\cdot\text{X}\cdot\text{Y}$, $\text{C}_5\text{H}_5\text{N}^+\cdot\text{X}\cdot\text{Y}$, $(\text{CH}_3)_2\text{CO}^+\cdot\text{X}\cdot\text{Y}$, $\text{NH}_4^+(\text{H}_2\text{O})_k(\text{NH}_3)_n$, and $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$. As to parts X and Y, they may be optional, still, in case of positive ions X and Y are usually H_2O and/or NH_3 .

The results obtained by virtue of simulations can be assessed from at least two aspects: first, the results of measurements obtained for steady-state composition of ions can be used; secondly, the ones describing temporary variations of the concentrations of ions can be applied. As recorded in Chapter 2, both of the comparisons may be necessary since being limited to one aspect only may result in an inadequate assessment. Unfortunately, in the earlier works it was not possible to make the both comparisons simultaneously: as it was discussed in Chapter 1, an advantage of the method used in the present work, as compared with the methods employed in the earlier works, was the ability of the method to yield information about both steady-state composition of ions and temporal variations of composition of ions.

To begin with, let us scan the results concerning the steady-state composition of ions.

In conformity with the results of the observations reviewed in Chapter 2, the main natural positive ions should be $\text{C}_5\text{H}_5\text{N}^+\cdot\text{X}\cdot\text{Y}$ and $\text{NH}_4^+(\text{H}_2\text{O})_k(\text{NH}_3)_n$, at which under some circumstances ions $\text{CH}_3\text{CN}^+\cdot\text{X}\cdot\text{Y}$ and/or $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$ can be met as well, all the same, the latter two ions are less abundant. As regards ions $\text{CH}_3\text{OH}^+\cdot\text{X}\cdot\text{Y}$ and $(\text{CH}_3)_2\text{CO}^+\cdot\text{X}\cdot\text{Y}$, composition of positive ions has indeed been found out to depend on the actual concentrations of both methanol and acetone, still, such ions are very exceptional in the natural air. Besides the ions mentioned above in this paragraph, sometimes a large number of unknown ions with masses up to about 500 a.m.u. has been observed.

Table 4.1. The steady-state abundances of positive ions.

Ions	Case								
	A	C	D	E	F	G	H	I	J
$\text{CH}_3\text{OH}^+\cdot\text{X}\cdot\text{Y}$	11	3	12	12	2	2	8	2	1
$\text{CH}_3\text{CN}^+\cdot\text{X}\cdot\text{Y}$	11	3	12	12	2	2	8	2	1
$\text{NH}_4^+(\text{H}_2\text{O})_k(\text{NH}_3)_n$	24	12	0	3	3	45	18	3	27
$\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$	24	2	16	17	1	4	45	4	7
$(\text{CH}_3)_2\text{CO}^+\cdot\text{X}\cdot\text{Y}$	3	80	3	4	1	1	2	1	36
$\text{C}_5\text{H}_5\text{N}^+\cdot\text{X}\cdot\text{Y}$	26	0	57	52	91	46	19	88	28

All abundances in per cents.

Legend to cases:

- A All concentrations of neutral gases according to Table 3.1;
- C The concentration of acetone increased 100 times;
- D The concentration of pyridine increased 100 times;
- E The concentration of pyridine increased 10 times;
- F Concentrations of pyridine and NH_3 increased 10 times;
- G The concentration of NH_3 increased 10 times;
- H The evolution of ions at a temperature of 243K, case C;
- I The evolution of ions at a temperature of 243K, case F;
- J : The evolution of ions at a temperature of 243K, the concentration of NH_3 increased 10 times, the concentration of acetone increased 100 times.

One can see, that the results of simulations reported in Table 4.1 accord quite well with the results of the observations, at least as to the general lines. Under normal conditions (case A) abundances of all the common ions should be nearly equal to one another. It is true that such situation has not actually been observed, still, on the other hand, evolution of positive ions should be quite sensitive to the actual concentrations of several neutral gases, as to simulations: an increase in the concentrations of both acetone, pyridine and NH_3 should result in certain ions becoming dominant. Besides, methanol and acetonitrile have analogical effects, but the respective results have not been included into Table 4.1. The results about the simulated variability of composition of ions presented in Table 4.1 can be compared with the results obtained by virtue of observations: in accordance with the latter ones, the natural composition of ions varies whereas ions $\text{C}_5\text{H}_5\text{N}^+\cdot\text{X}\cdot\text{Y}$ are the most ordinary ones, but ions $\text{NH}_4^+(\text{H}_2\text{O})_k(\text{NH}_3)_n$ are also quite common, and sometimes several other ions can occur as well. Therefore, case A can be regarded as a "central point", at which the special cases reported

in Table 4.1 can be in principle considered correspondent to the individual cases observed by virtue of measurements. True, although this approach is quite rough, any quantitative criterion can not be defined here because the actual composition of neutral environment has remained ordinarily unknown. Thus, the results of observations of steady-state composition of ions enable only a comparatively rough assessment of the model.

To continue the assessment, let us now scan the available data about the temporal variations of composition of ions: some results obtained by virtue of the present model are presented in Tables 4.2 ja 4.3. For comparison, mainly the results reviewed in Articles 2.4.5 and 2.3.2 will be applied.

Table 4.2. The abundances of positive ions at the age of about 1 s.

Ions	Case									
	A	C	D	E	F	G	H	I	J	
$\text{CH}_3\text{OH}^+\cdot\text{X}\cdot\text{Y}$	1	1	1	1	1	1	0	0	0	
$\text{CH}_3\text{CN}^+\text{X}\cdot\text{Y}$	1	1	1	1	1	1	0	0	0	
$\text{C}_3\text{H}_5\text{N}^+\cdot\text{X}\cdot\text{Y}$	0	0	2	0	3	0	0	1	0	
$(\text{CH}_3)_2\text{CO}^+\cdot\text{X}\cdot\text{Y}$	0	20	0	0	0	0	0	0	8	
$\text{NH}_4^+(\text{H}_2\text{O})_k(\text{NH}_3)_n$	3	3	2	3	27	29	1	12	12	
$\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$	95	75	94	95	69	69	98	86	79	

All abundances in per cents.

Legend to cases: see Table 4.1.

As we can see from Tables 4.2 and 4.3, at the age of ions near 1 s, mainly ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$ occur, other ions become substantial in case of more aged ions. As to the age of about 1 s, ions $\text{NH}_4^+(\text{H}_2\text{O})_k(\text{NH}_3)_n$ should be significantly less abundant than $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$, but the part of the former ions should increase along with an increase in the age of ions. Consequently, at the ages between about 1 s and 10 s, the nature of positive ions should change. For comparison, at the age of about some hundreds of milliseconds both ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$ and ions $\text{NH}_4^+(\text{H}_2\text{O})_k(\text{NH}_3)_n$ have been observed (Eisele, 1988). Therefore, the essence of the change in the nature found out by means of simulations should be correct, nevertheless the actual age of the change requires further justification. On the one hand, a change in the nature of positive ions should indeed take place at the age of about some seconds, and not before, as it can be learned from the results obtained by virtue of mobility spectrometry. On the other hand, according to the work (Perkins and Eisele, 1984) the respective change should take place long before 1 s, since at the age of about 1 s, ions $\text{NH}_4^+(\text{H}_2\text{O})_k(\text{NH}_3)_n$ have been observed to be already dominant. Consequently, we have to do with somewhat

contradictory results, and that is why the quantitative assessment of the model can not be terminated. Still, it seems as if the qualitative behaviour of the model is correct. As regards the quantitative consideration, the experiments described above might be incomparable because of different conditions.

Table 4.3. The abundances of positive ions at the age of about 3 s.

Ions	Case								
	C	A	D	E	F	G	H	I	J
$\text{CH}_3\text{OH}^+\cdot\text{X}\cdot\text{Y}$	2	2	2	2	1	1	1	1	1
$\text{CH}_3\text{CN}^+\cdot\text{X}\cdot\text{Y}$	2	2	2	2	1	1	1	1	1
$\text{C}_5\text{H}_5\text{N}^+\cdot\text{X}\cdot\text{Y}$	0	0	9	3	18	3	0	11	1
$(\text{CH}_3)_2\text{CO}^+\cdot\text{X}\cdot\text{Y}$	1	46	1	1	0	0	0	0	18
$\text{NH}_4^+(\text{H}_2\text{O})_k(\text{NH}_3)_n$	9	7	2	6	36	49	4	19	26
$\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$	86	44	84	86	43	46	94	69	54

All abundances in per cents.

Legend to cases: see Table 4.1.

As it can be seen from Tables 4.2 and 4.3, an increase in the concentrations of pyridine, acetone, and NH_3 results in a certain change of composition of ions at the age of about a few seconds. For comparison, the results concerning the ions at the age of about 1 s, reviewed in Article 2.4.5, have shown following effects: in case of the increased concentration of pyridine, the part of the ions with larger mobilities increased; the data about the effects due to an increase in the concentration of NH_3 have been quite discrepant, nevertheless, some results have shown an increase of abundance of the ions with smaller mobilities; in case of acetone the respective changes of spectrum have not been specified.

As regards acetone, here, the results obtained are in significant conformity with each other: an increase in the concentration of acetone induces a new class of ions to become substantial (cases A and C). At the same time, the new class of ions may indeed induce the change of mobility spectrum observed in the works reviewed in Article 2.4.5, that is in the manner described in Article 2.4.1.

As for pyridine, the effects expected on the ground of the model should be somewhat weaker: although an increase in the concentration induces a new class of ions that may lead to a change in mobility spectrum, the part of the new ions remains too small. As it can be seen in Figure 2.4, an increased concentration of pyridine should be followed by an increase of the peak corresponding to lighter ions, at the same time the peak conditioned by heavier ions should decrease. In accordance with Tables 4.2 and 4.3, an increase in one class of ions is indeed accompanied by a decrease in another, all the same, ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$ included

into the model are, as a matter of fact, not heavier than ions $C_5H_5N^+ \cdot X \cdot Y$. On the other hand, ions $H_3O^+(H_2O)_k$ included into the model may be too light as discussed in Article 2.2, due to which the change in the nature of ions expected on the ground of the model may, in principle, be correct. Nevertheless, the results presented in Tables 4.2 and 4.3 are not in good accordance with some another data: in conformity with the results of simulations, ions $C_5H_5N^+ \cdot X \cdot Y$ should occur together with ions $NH_4^+(H_2O)_k(NH_3)_n$, but the latter should lead to an another peak in mobility spectrum, which has not been observed yet. The situation remains unchanged also in case of significantly increased concentrations of pyridine, since an increase in the concentration of pyridine first of all has an effect when accompanied by an increase in the concentration of NH_3 (cases D and E). At the same time, the results of measurements have not implied at the effects conditioned by pyridine to depend on the actual concentration of NH_3 . The discrepancy mentioned last can be eliminated assuming that actually not a replacement of ions $H_3O^+(H_2O)_k$ by ions $C_5H_5N^+ \cdot X \cdot Y$ takes place but a replacement of ions $NH_4^+(H_2O)_k(NH_3)_n$ by ions $C_5H_5N^+ \cdot X \cdot Y$ proceeds. On the other hand, the assumption would involve ions $NH_4^+(H_2O)_k(NH_3)_n$ to be met long before the age of about 1 s, yet, this presumption has not been universally endorsed. Moreover, available data imply that ions $H_3O^+(H_2O)_k$ should be still heavier than ions $NH_4^+(H_2O)_k(NH_3)_n$, therefore, ions $H_3O^+(H_2O)_k$ should be more appropriate as to the role of earlier ions of the process.

Consequently, as regards pyridine, it seems as if the model is in a satisfactory qualitative accordance with the results of measurements, all the same, the quantitative accordance should be better. In this case, it looks as if ions $NH_4^+(H_2O)_k(NH_3)_n$ are rather superfluous, and therefore, it can be supposed that certain unknown reactions proceed, converting ions $H_3O^+(H_2O)_k$ directly into ions $C_5H_5N^+ \cdot X \cdot Y$, that is, without ions $NH_4^+(H_2O)_k(NH_3)_n$ to participate.

Next, let us consider the effects conditioned by the variations in the concentration of NH_3 . According to the model, a tenfold increase in the concentration induces substantial changes in the nature of positive ions (cases A and F). As regards the results of measurements, they are quite discrepant: most of the works have found composition of positive ions significantly independent from the concentration of NH_3 , although some different results are available as well (see Figure 2.4). According to the model, NH_3 should have a significantly strong effect, which may not become apparent at a certain age of ions only in case the formation of ions $NH_4^+(H_2O)_k(NH_3)_n$ has already been terminated before the age of interest. If so, either the concentration of NH_3 considered normal in the model has been actually underrated, or the reactions producing ions $NH_4^+(H_2O)_k(NH_3)_n$ are, as a matter of fact, significantly faster than they should be in conformity with the known data. Nevertheless, the potentiality that the formation of ions $NH_4^+(H_2O)_k(NH_3)_n$ would be completed long before the age of about 1 s is questionable: on the one hand, the results of observations obtained at the ages of ions being about some hundreds of milliseconds have indeed shown both ions $H_3O^+(H_2O)_k$ and ions $NH_4^+(H_2O)_k(NH_3)_n$ as reviewed above, that is why, it could be guessed that the formation of ions $NH_4^+(H_2O)_k(NH_3)_n$ proceeds at the age of about some hundreds of milliseconds; on the other hand, mobility spectrums have not shown any change in the nature of positive ions due to the

ageing of ions as far as the ages between 0.2 s and 2 s are concerned. Therefore, it seems as if the guess about the formation of ions $\text{NH}_4^+(\text{H}_2\text{O})_k(\text{NH}_3)_n$ namely at the age of some hundreds of milliseconds is quite questionable. Accordingly, any conclusion can not be made because of the discrepancy of data, all the same, it is clear that the strong effect of NH_3 obtained by means of the model exceeds the expectations on the ground of the respective results of observations.

Proceeding from Chapter 2, evolution of positive ions depends on the concentrations of several other neutral gases. As regards the model, in principle the situation is as follows: first, several gases, such as acetonitrile or methanol, have effects (not presented here) analogical to the one obtained in case of acetone, consequently, the results obtained by means of the model are in qualitative accordance with the results obtained by virtue of observations; secondly, several effects observed (e.g., due to amines) can not be simulated correctly because of shortage of necessary data.

Next let us deal with masses of the ions. In case of ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$ obtained by virtue of the model, the main individual ion species should be $\text{H}_3\text{O}^+(\text{H}_2\text{O})_5$ and $\text{H}_3\text{O}^+(\text{H}_2\text{O})_6$ with masses of 109 a.m.u. and 127 a.m.u. respectively; in case of ions $\text{NH}_4^+(\text{H}_2\text{O})_k(\text{NH}_3)_n$, the main individual ion species should be $\text{NH}_4^+(\text{H}_2\text{O})_4$ and $\text{NH}_4^+(\text{H}_2\text{O})_5$ with masses of 90 a.m.u. and 108 a.m.u. respectively, in case of ions $\text{C}_5\text{H}_5\text{N}^+\text{X}\cdot\text{Y}$, there should mainly be ions $\text{C}_5\text{H}_5\text{N}^+(\text{H}_2\text{O})_5$ with mass 169 a.m.u. For comparison, the mobilities of positive ions are about $1.5 \text{ cm}^2/(\text{V}\cdot\text{s})$, which should, in conformity with Formula (1.2), be equivalent to masses of about 140 a.m.u. Consequently, the masses of ions $\text{C}_5\text{H}_5\text{N}^+\text{X}\cdot\text{Y}$ are quite close to the masses supposed on the ground of mobility spectrums of positive ions; unfortunately, the same can not be said about ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$ and $\text{NH}_4^+(\text{H}_2\text{O})_k(\text{NH}_3)_n$. Therefore, the latter two ions should actually be clustered more heavily than the ions included into the present model. Unfortunately, the more heavily clustered ions can not be included into the model because of shortage of necessary thermodynamic data.

The discussion presented in this Article can be summarized as follows: the present model of the evolution of positive ions yields the results oftentimes significantly close to the results obtained by means of measurements, still, certain discrepancies appear particularly when ions at the age of about 1 s are concerned, likewise, the quantitative accordance is not sure. Most of the discrepancies are likely to be due to shortage or inaccuracy of necessary initial data.

Besides, some results about evolution of ions at lower temperatures are presented as well: it seems as if at lower temperatures the ions of earlier stages of evolution (ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$) are more abundant. Unfortunately, this result can not be assessed because the measurement results about the dependence of composition of ions on temperature are actually absent.

In addition, some illustrative results are depicted in Figures 4.1 and 4.2.

The content of Figure 4.1 is somewhat analogical to that of Tables 4.2 and 4.3: in Tables 4.2 and 4.3 the relative parts of ions at the ages of 1 s and 3 s were presented for many cases, at the same time in Figure 4.1 the all-scale time-variations of relative parts of ions are depicted for case A only. As we can see from Figure 4.1, buffer ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k$ become dominant already at very early stages of the evolution of ions, henceforth, the buffer ions stay dominant

until the age of about few seconds when terminal ions become apparent. Figure 4.2 has the same content as Table 4.1 has, only the form of presentation of data is more expressive.

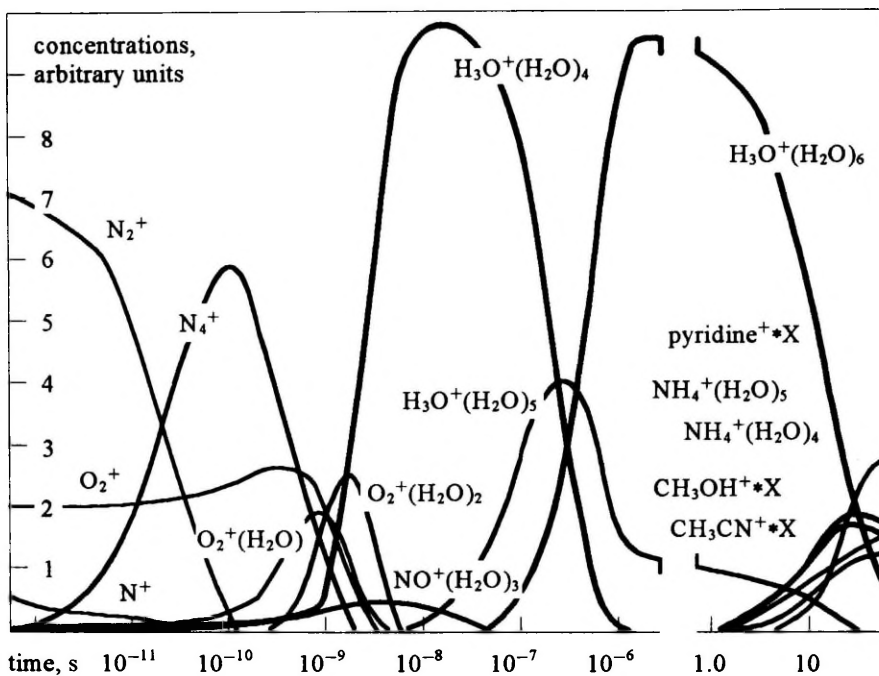


Figure 4.1. Time-dependence of concentrations of positive ions. Case A; (legend to cases: see Table 4.1).

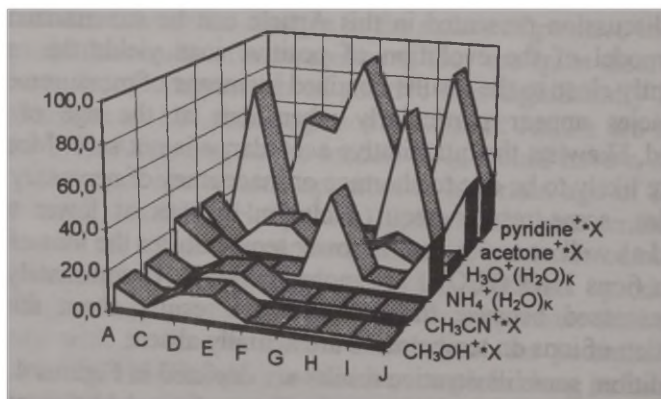


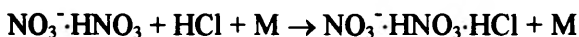
Figure 4.2. Dependence of steady-state abundances of positive ions on concentrations of some neutral gases; (legend to cases: see Table 4.1).

4.2. Evolution of negative ions

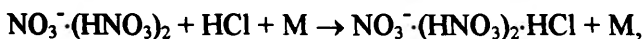
Some quantitative results obtained by virtue of simulation of the evolution of negative ions are presented in Tables 4.4, 4.5, and 4.6; some illustrative results are depicted in Figures 4.3 and 4.4. In the first place, let us consider certain common problems not evident in the Tables but resulting from the model presented in Article 2.5.5.2.

First, in conformity with the model a large number of ions $\text{NO}_3^-(\text{HNO}_3)_k \cdot (\text{HCl})_n$ should be formed. The result accords with the results of measurements regarding the information reviewed in Article 2.4.4: composition of negative ions has indeed been found to be significantly dependent on the concentration of HCl. True, the results of measurements contain only a qualitative description of the effects, ions $\text{NO}_3^-(\text{HNO}_3)_k \cdot (\text{HCl})_n$ have not been mentioned anywhere, but according to the discussion presented in Article 2.5.5.2 these ions are very likely to occur because there is very few data about other ions which may be regarded as the ions due to HCl. On the other hand, the results concerning a large number of ions $\text{NO}_3^-(\text{HNO}_3)_k \cdot (\text{HCl})_n$ do not accord with several other results: as to natural air, the ions have not been observed, according to the observations either ions $\text{NO}_3^-(\text{HNO}_3)_n(\text{H}_2\text{O})_m$ or ions $\text{HSO}_4^- \cdot \text{X} \cdot \text{Y}$, where X and Y denote either H_2O , H_2SO_4 or HNO_3 molecules, should be dominant. True, the observed ions $\text{NO}_3^- \cdot \text{X} \cdot \text{Y}$ might, in effect, contain not only H_2O and/or HNO_3 molecules, but also HCl molecules because of the problems of identification of ions described in Chapter 2. All the same, the fact deserves to be mentioned: the ions including HCl molecules have been reported only very exceptionally. For comparison, the model results in the composition of ions containing ions $\text{NO}_3^-(\text{HNO}_3)_n(\text{H}_2\text{O})_m$ less than ions $\text{NO}_3^-(\text{HNO}_3)_k \cdot (\text{HCl})_n$, which is quite unlike as to the results of observations.

The mathematical reason of the problem is obvious: the large number of ions $\text{NO}_3^-(\text{HNO}_3)_k \cdot (\text{HCl})_n$ is conditioned by very fast reactions



and

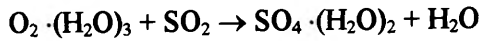
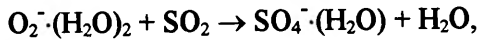
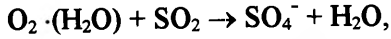


introduced in Article 2.5.5.2. The data about these reactions have been taken from (Ikezoe, 1987), the author of the present work can not assess these data. Anyway, the problems described above are mainly due to these two reactions.

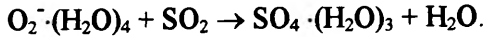
In order to get a better accordance with the results of observations, we will use the decreased concentration of HCl: the concentration considered normal is henceforth equal to $1.2 \times 10^7 \text{ cm}^{-3}$. Actually, the concentration should be decreased about 10 more times, as it can be seen from the comparison between case A and case B. Nevertheless, in the present work we confine ourselves to the decrease mentioned above, since in the opposite case the concentration of HCl would be too different as compared with the concentration found out in Chapter 3. As a matter of fact, concentrations of HCl are quite well known (see Chapter 3), therefore, the decrease applied above can not be sufficiently motivated: it is true that in this way the model becomes closer to the other results, still, this is the sole motivation. In effect, the set of the data about ion-molecule reactions employed in

the present work should be improved, yet, this can not be done because of shortage of data.

The common problem discussed last is not the last one: namely, the model results in superfluous amount of ions $\text{NO}_2^- \cdot \text{X} \cdot \text{Y}$. As regards the mathematical aspect, the situation is due to the following very fast reactions:



and



The reactions produce ions $\text{SO}_4^- \cdot (\text{H}_2\text{O})_k$, which, in their turn, will be transformed both into ions $\text{NO}_2^- \cdot \text{X} \cdot \text{Y}$ (about 70%), and into ions $\text{NO}_3^- \cdot \text{X} \cdot \text{Y}$ (about 30%). Respective reactions were introduced in Article 2.5.5.2, and the author of the present work can not assess them. Nevertheless, it is clear that the reactions result in a superfluous number of ions $\text{NO}_2^- \cdot \text{X} \cdot \text{Y}$. As we have no additional information about the reactions, the discrepancy can be eliminated in two ways: first, we can exclude the very fast reactions producing ions $\text{SO}_4^- \cdot (\text{H}_2\text{O})_k$; secondly, we can decrease the concentration of SO_2 . In the present work the decreased concentration of SO_2 is used: the concentration considered normal is henceforth equal to $3,0 \times 10^8 \text{ cm}^{-3}$. As to motivation, this method can be motivated only by the fact, that, due to it the outcomes of the model become closer to the results obtained by means of measurements.

The changes described above in this Article result in a new normal case of the model outcomes of which are presented in Tables 4.4 – 4.6 as case A.

Next, let us discuss the outcomes presented in Table 4.4. As we can see, provided that the discrepancies discussed above are discarded, the outcomes are quite close to the results of observations of the natural composition of negative ions. True, ions $\text{NO}_3^- \cdot (\text{HNO}_3)_k \cdot (\text{H}_2\text{O})_k$ should be substantial both according to model and according to the results of observations. As regards observations, besides ions $\text{NO}_3^- \cdot (\text{HNO}_3)_k \cdot (\text{H}_2\text{O})_k$, ions $\text{HSO}_4^- \cdot \text{X} \cdot \text{Y}$ should be substantial, whereas X and Y denote either H_2O , HNO_3 or H_2SO_4 molecules. As to the model, the latter ions become substantial in case of increased concentrations of H_2SO_4 . In case the concentration of H_2SO_4 is equal to $4,0 \times 10^8 \text{ cm}^{-3}$, the part of ions $\text{HSO}_4^- \cdot \text{X} \cdot \text{Y}$ makes up about 26%, and it increases along with a further increase in the concentration of H_2SO_4 . In order to conclude the quantitative assessment, the actual concentrations of H_2SO_4 are to be known. Unfortunately, the actual concentrations of H_2SO_4 are not well known, as shown in Chapter 3. Consequently, with certain reservations not only the concentration derived in Chapter 3, but also the concentration of $4,0 \times 10^8 \text{ cm}^{-3}$ can be considered normal. If so, the outcomes presented as case C can be regarded as the outcomes of the normal case, which also accord well with the results of observations: true, both ions $\text{HSO}_4^- \cdot \text{X} \cdot \text{Y}$ and ions $\text{NO}_3^- \cdot (\text{HNO}_3)_k \cdot (\text{H}_2\text{O})_k$ have been found out by observations, whereas the observed variations of their relative abundances can be simulated by means of respective variations in the concentration of H_2SO_4 .

Nevertheless, the conclusions are mostly qualitative, the quantitative assessment can not be terminated because of shortage of data.

Table 4.4. The steady-state abundances of negative ions.

Ions	Case								
	A	B	C	D	E	F	G	H	I
$\text{CO}_3^- \cdot (\text{H}_2\text{O})_k$	0	0	0	0	0	0	0	1	0
$\text{O}_2^- \cdot (\text{H}_2\text{O})_k$	1	1	1	1	0	1	0	4	0
$\text{HCO}_3^- \cdot (\text{H}_2\text{O})_k$	1	1	1	1	1	1	1	1	0
$\text{Cl}^- \cdot (\text{H}_2\text{O})_k$	0	0	0	0	0	0	0	0	1
$\text{HSO}_4^- \cdot \text{X} \cdot \text{Y}$	0	0	26	1	0	0	1	0	1
$\text{SO}_4^- \cdot (\text{H}_2\text{O})_k$	0	0	0	0	0	3	0	0	0
$\text{NO}_2^- \cdot (\text{H}_2\text{O})_k$	15	15	15	9	85	42	15	10	1
$\text{NO}_3^- \cdot (\text{HNO}_3)_k \cdot (\text{H}_2\text{O})_k$	55	78	38	4	9	36	32	73	15
$\text{NO}_3^- \cdot \text{HCl} \cdot (\text{HNO}_3)_k \cdot (\text{H}_2\text{O})_k$	27	4	18	84	4	18	51	10	82

All abundances in per cents.

Legend to cases:

- A All concentrations of neutral gases according to Table 3.1 and Paragraph 4.3;
- B The concentration of HCl decreased 10 times;
- C : The concentration of H_2SO_4 increased 100 times;
- D The concentration of HNO_3 increased 100 times;
- E The concentration of NO_2 increased 100 times;
- F The concentration of SO_2 increased 100 times;
- G The concentration of water decreased 2 times;
- H The concentration of water increased 2 times;
- I The evolution of ions at temperature 243K, case A.

Next, let us assess the outcomes describing the time-dependence of the concentrations; the outcomes are presented in Tables 4.5 and 4.6. For comparison, we will mainly apply the results reviewed in Article 2.4.4.

Conformably to the results reviewed in Article 2.4.4, at the ages of ions between about 0.2 s and 1 s, the nature of negative ions should change: the earlier class of ions should be replaced by a new class of ions, whereas the actual age for the process to take place depends on the concentration of water (see also Figure 2.1).

Table 4.5. The abundances of negative ions at the age of about 0.25 s.

Ions	Case								
	A	B	C	D	E	F	G	H	I
$\text{CO}_3^-(\text{H}_2\text{O})_k$	15	15	15	7	0	13	23	5	21
$\text{O}_2^-(\text{H}_2\text{O})_k$	69	69	69	69	2	44	23	89	23
$\text{HCO}_3^-(\text{H}_2\text{O})_k$	1	1	1	1	1	1	1	1	0
$\text{Cl}^-(\text{H}_2\text{O})_k$	0	0	0	1	0	0	0	0	0
$\text{HSO}_4^- \cdot \text{X} \cdot \text{Y}$	0	0	0	0	0	0	0	0	0
$\text{SO}_4^-(\text{H}_2\text{O})_k$	0	0	0	0	0	29	1	0	0
$\text{NO}_2^-(\text{H}_2\text{O})_k$	4	4	4	4	89	4	14	1	13
$\text{NO}_3^-(\text{HNO}_3)_k \cdot (\text{H}_2\text{O})_k$	11	11	11	18	9	10	40	4	41

All abundances in per cents.

Legend to cases: See Table 4.4.

A certain change in the nature of negative ions can also be observed as compared the results in Table 4.5 with the results in Table 4.6: true, the earlier ions $\text{O}_2^-(\text{H}_2\text{O})_k$ are replaced by ions $\text{NO}_3^-(\text{HNO}_3)_k \cdot (\text{H}_2\text{O})_k$, and the actual age for the process to take place depends on the concentration of water, as it can be seen from cases G and H. As regards the individual ion species, most of ions $\text{O}_2^-(\text{H}_2\text{O})_k$ are actually in form $\text{O}_2^-(\text{H}_2\text{O})_5$, most of ions $\text{NO}_3^-(\text{HNO}_3)_k \cdot (\text{H}_2\text{O})_k$ are either in form $\text{NO}_3^-(\text{H}_2\text{O})_3$ or $\text{NO}_3^-(\text{H}_2\text{O})_2$. As the masses of the respective ion species are 122 a.m.u., 116 a.m.u., and 98 a.m.u., the change in the nature of ions should be accompanied by a decrease in the masses of ions, which, likewise, accords with the results reviewed in Article 2.4.4. On the other hand, proceeding from the results depicted in Figure 2.1, and from Formula (1.2), the mobilities of the respective classes of ions should be about $1.8 \text{ cm}^2/(\text{V}\cdot\text{s})$ and $2.0 \text{ cm}^2/(\text{V}\cdot\text{s})$, which should be equivalent to masses of about 90 a.m.u. and 65 a.m.u. Consequently, the masses obtained by virtue of the model exceed the ones expected on the ground of the data depicted in Figure 2.1. Nevertheless, Formula (1.2) does not represent the exact nexus between the mobility and the mass of an ion as described in Chapter 2, therefore, the mobilities mentioned last may, in effect, be conditioned not by the masses expected last, but by some other masses, that is why, the ion species expected on the ground of the model may be right. Moreover, the actual number of water molecules clustered around the core of an ion strongly depends both on the temperature and on the concentration of water, therefore, the differences in masses mentioned above may actually be due to

different conditions. Thus, it seems as if the outcomes of the present model of negative ions are comparatively close to the results of measurements, as to the ageing of ions and effects conditioned by variations in the concentration of water.

Next, let us scan the data about effects conditioned by variations in the concentrations of certain neutral gases. As it is known from Article 2.4.4, composition of ions at the age of about 1 s significantly depends on the concentrations of NO_2 , HCl , certain sulfur oxides, chloracetic acid, and several amines; less substantial effects can be observed due to the large number of gases, e.g. HNO_3 ; whereas H_2SO_4 has been found to have no significant effect on the composition of ions at the age of about 1 s.

Effects conditioned by variations in the concentrations of several gases have been studied also by means of the present model, some outcomes are presented in Tables 4.5 and 4.6. Differently from Table 4.4, ions $\text{Cl}^-(\text{H}_2\text{O})_k$ have not been included in Tables 4.5 and 4.6 in form of a separate row, because the actual concentrations of ions $\text{Cl}^-(\text{H}_2\text{O})_k$ were very low. Instead of that, "ions" $\text{Cl}^-\cdot\text{X}\cdot\text{Y}$ have been introduced denoting both ions $\text{NO}_3^-\cdot\text{HCl}\cdot(\text{HNO}_3)_k\cdot(\text{H}_2\text{O})_k$ and ions $\text{Cl}^-(\text{H}_2\text{O})_k$.

Table 4.6. The abundances of negative ions at the age of about 1 s.

Ions	Case								
	A	B	C	D	E	F	G	H	I
$\text{CO}_3^-(\text{H}_2\text{O})_k$	15	15	15	3	0	7	1	12	1
$\text{O}_2^-(\text{H}_2\text{O})_k$	26	25	25	26	0	4	1	68	0
$\text{HCO}_3^-(\text{H}_2\text{O})_k$	1	1	1	1	1	1	1	1	0
$\text{Cl}^-\cdot\text{X}\cdot\text{Y}$	0	0	0	11	0	0	2	0	2
$\text{HSO}_4^-\cdot\text{X}\cdot\text{Y}$	0	0	0	0	0	0	0	0	0
$\text{SO}_4^-(\text{H}_2\text{O})_k$	1	1	1	1	0	42	0	0	0
$\text{NO}_2^-(\text{H}_2\text{O})_k$	11	11	11	11	90	14	18	3	16
$\text{NO}_3^-(\text{HNO}_3)_k\cdot(\text{H}_2\text{O})_k$	47	47	47	48	9	32	78	17	81

All abundances in per cents.

Legend to cases: See Table 4.4.

As we can see from Tables 4.5 and 4.6, variations in the concentrations of both NO_2 and SO_2 have remarkable effects on composition of ions. In the first case a large number of ions $\text{NO}_2^-(\text{H}_2\text{O})_k$ is formed, while the concentrations of other ions become negligible (case E); in the second case a considerable amount of ions $\text{SO}_4^-(\text{H}_2\text{O})_k$ is formed, whereas the latter ions are indeed heavier as compared with the other ions in the system. The result accords quite well with the effect

depicted in Figure 2.3 (case F). As regards the strong effects conditioned by HCl observed by measurements, similar effects result from the model as well: as discussed above, the effects due to HCl are even too strong. Next, HNO₃ has an effect, although weaker, indeed: an increase in the concentration of HNO₃ induces an increase in abundance of ions Cl⁻·X·Y (case D). As to the influence due to H₂SO₄, the respective influence on ions which are about 1 s of age, can be considered negligible (see case C). Consequently, all the effects presented in Tables 4.5 and 4.6 accord, in principle, with the ones found out by virtue of measurements. Nevertheless, certain effects reviewed in Article 2.4.4 can not be simulated nowadays because of shortage of the data about necessary ion-molecule reactions.

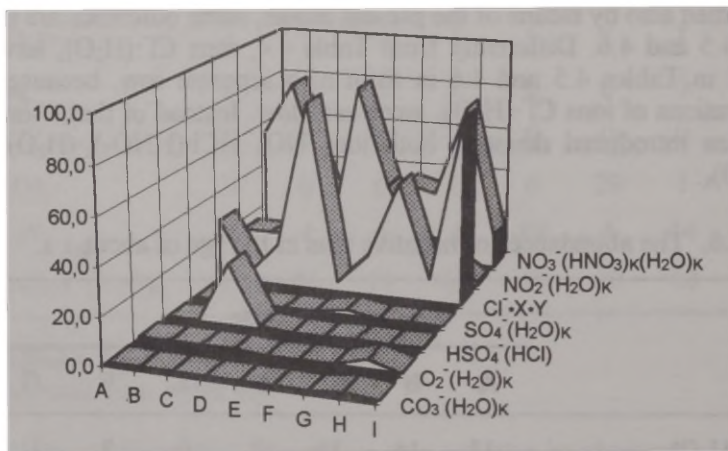


Figure 4.3. Dependence of steady-state abundances of negative ions on the concentrations of some neutral gases (legend to cases: see Table 4.1).

In addition, Tables 4.4 – 4.6 present the results describing the composition of ions which should be at lower temperatures (case I). At lower temperatures, the terminal ions should be formed faster: already at the ages of about 1 s the main ions should be $\text{NO}_3^-\cdot(\text{HNO}_3)_k\cdot(\text{H}_2\text{O})_k$, while in the steady state, ions $\text{NO}_3^-\cdot\text{HCl}\cdot(\text{HNO}_3)_k\cdot(\text{H}_2\text{O})_k$ should be dominant. Unfortunately, these outcomes can not be assessed because of shortage of respective measurement results.

Besides, some illustrative results are depicted in Figures 4.3 and 4.4.

The contents of Figure 4.3 and Table 4.4 are identical. Similarly, Figure 4.4 has the same content as Table 4.6 has, only the forms of presentation of data are more expressive in the latter variants. The fact that the effects due to the changes in the concentration of neutral gases depend on the age of the ions, becomes evident specially while comparing Figure 4.3 with Figure 4.4.

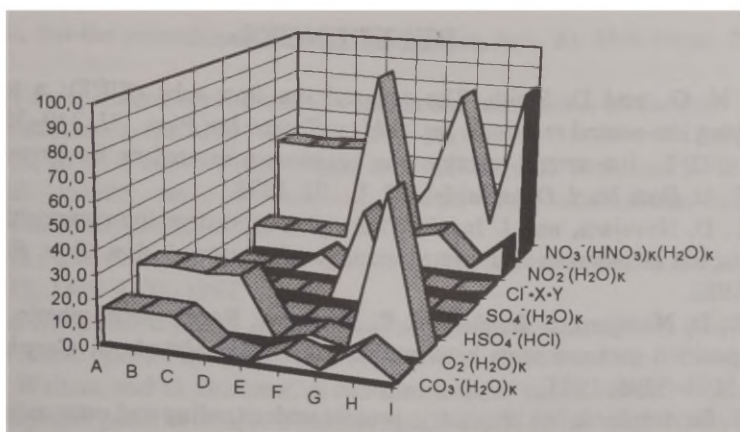


Figure 4.4. Dependence of abundances of negative ions of the age of about 1 s on concentrations of some neutral gases (legend to cases: see Table 4.1).

The results of the model of negative ions can be summarized as follows. On the one hand, several outcomes of the model are quite close to the results obtained by measurements, at least as to qualitative aspects. On the other hand, certain problems discussed above remain unsolved. Nevertheless, it seems as if the core of the present model is comparatively accurate, it would be quite easy to improve the model as soon as the new data of interest becomes available.

REFERENCES

- Adams, N. G., and D. Smith, The selected ion flow tube (SIFT); a technique for studying ion-neutral reactions, *Int. J. Mass Spectr. Ion Phys.*, **21**, 349–359, 1976.
- Albritton, D. L., Ion-neutral reaction rate constants measured on flow reactors through 1977, *At. Data Nucl. Data Tables*, **22**, 1–101, 1978.
- Arijs, E., D. Nevejans, and J. Ingels, Stratospheric positive ion composition measurements, ion abundances and related trace gas detection, *J. Atm. Terr. Phys.*, **44**, 43–53, 1982.
- Arijs, E., D. Nevejans, J. Ingels, and P. Frederick, Recent stratospheric negative ion composition measurements between 22- and 45-km altitude, *J. Geophys. Res.*, **90**, D4, 5891–5896, 1985.
- Arijs, E., Stratospheric ion chemistry: present understanding and outstanding problems, *Planet. Space Sci.*, **40**, 2/3, 255–270, 1992.
- Arlander, D. W., D. R. Cronn, J. C. Farmer, F. A. Menzia, and H. H. Westberg, Gaseous oxygenated hydrocarbons in the remote marine troposphere, *J. Geophys. Res.*, **95**, D10, 16391–16403, 1990.
- Arnold, F., Multi-ion complexes in the stratosphere—implications for trace gases and aerosol, *Nature*, **284**, 610–611, 1980.
- Arnold, F., G. Henschen, and E. E. Ferguson, Mass spectrometric measurements of fractional ion abundances in the stratosphere — positive ions, *Planet. Space Sci.*, **29**, 185–193, 1981a.
- Arnold, F., R. Fabian, E. E. Ferguson, and W. Joos, Mass spectrometric measurements of fractional ion abundances in the stratosphere—negative ions, *Planet. Space Sci.*, **29**, 195–203, 1981b.
- Arnold, F., A. A. Viggiano, and H. Schlager, Implications for trace gases and aerosols of large negative ion clusters in the stratosphere, *Nature*, **297**, 371–376, 1982.
- Arnold, F., H. Heimann, and K. Oberfrank, First composition measurements of positive ions in the upper troposphere, *Planet. Space Sci.*, **32**, 12, 1567–1576, 1984.
- Atkins, P. W., *Physical chemistry*, Oxford University Press, 1986.
- Atkinson, Roger, Sara M. Aschmann, Arthur M. Winer, and James J. Pitts, Jr., Kinetics of the gas phase reactions of NO₃ radicals with a series of dialkanes, cycloalkanes, and monoterpenes at 295±1 K, *Environ. Sci. Technol.*, **18**, 370–375, 1984.
- Atkinson, R., D. L. Baulch, R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, and J. Troe, Evaluated kinetic and photochemical data for atmospheric chemistry, supplement III, *J. Phys. Chem. Ref. Data*, **18**, 2, 881–1095, 1989a.
- Atkinson, R., D. L. Baulch, R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, and J. Troe, Evaluated kinetic and photochemical data for atmospheric chemistry, supplement III, *Int. J. Chem. Kin.*, **21**, 115–150, 1989b.
- Barnard, W. R., M. O. Andreae, W. E. Watkins, H. Bingemer, and H.-W. Georgii, The flux of dimethylsulfide from the oceans to the atmosphere, *J. Geophys. Res.*, **87**, C11, 8787–8793, 1982.
- Batcher and Charlson, 1984: Батчер, С. и Р. Чарлсон, *Введение в химию атмосферы*, Москва: Мир, 1984.
- Bates, D. R., Temperature dependence of rate coefficients for ter-molecular association, *J. Chem. Phys.*, **83**, 9, 4448–4450, 1985a.

- Bates, D. R., Ion-ion recombination in an ambient gas, *Adv. At. Mol. Phys.*, 20, 1–40, 1985b.
- Bates, D. R., Temperature dependence of termolecular association of diatomic ions with diatomic molecules, *J. Chem. Phys.*, 90, 1, 87–90, 1989.
- Baulch, D. L., R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, J. Troe, and R. T. Watson, Evaluated kinetic and photochemical data for atmospheric chemistry, *J. Phys. Chem. Ref. Data*, 9, 2, 295–471, 1980.
- Becker, K. H., and A. Ionescu, Acetonitrile in the lower troposphere, *Geophys. Res. Lett.*, 9, 12, 1349–1351, 1982.
- Beig, G., and D. K. Chakrabarty, A theoretical model of the stratospheric positive ions, *Indian J. Radio Space Phys.*, 16, 313–317, 1987.
- Beig, G., S. Walters, and G. Brasseur, A two-dimensional model of ion composition in the stratosphere: positive ions, *J. Geophys. Res.*, 98, D7, 12767–12773, 1993a.
- Beig, G., S. Walters, and G. Brasseur, A two-dimensional model of ion composition in the stratosphere: negative ions, *J. Geophys. Res.*, 98, D7, 12775–12781, 1993b.
- Bonsang, B., D. Martin, G. Lambert, M. Kanakidou, J. C. Le Roulley, and G. Senequier, Vertical distribution of non methane hydrocarbons in the remote marine boundary layer, *J. Geophys. Res.*, 96, D4, 7313–7324, 1991.
- Brasje and Solomon, 1987: Брасье, Т. и С. Соломон, *Аэрономия средней атмосферы*. Ленинград: Гидрометеониздат, 1987.
- Brasseur, G., and A. Chatel, Modelling of stratospheric ions: a first attempt, *Ann. Geophys.*, 1, 2, 173–185, 1983.
- Brasseur, G., R. Zellner, A. De Rudder, and E. Arijs, Is hydrogen cyanide (HCN) a progenitor of acetonitrile (CH₃CN) in the atmosphere?, *Geophys. Res. Lett.*, 12, 3, 117–120, 1985.
- Bufler, U., and K. Wegmann, Diurnal variation of monoterpene concentrations in open-top chambers and in the Welzheim Forest air, F. R. G., *Atm. Env.*, 25A, 2, 251–256, 1991.
- Cabane, M., and M. R. Milani, Study of the mobility of small ions in air, *Res. Lett. Atm. Electricity*, 3, 1983.
- Caledonia, G. E., A survey of the gas-phase negative ion kinetics of inorganic molecules. Electron attachment reactions, *Chem. Rev.*, 75, 3, 333–351, 1975.
- Carney, T. A., and J. Fishman, A one-dimensional photochemical model of the troposphere with a trade-wind boundary-layer parametrization, *Tellus*, 38B, 127–143, 1986.
- Carroll, D. I., I. Dzidic, R. N. Stillwell, K. D. Haegele, and E. C. Horning, Atmospheric pressure ionization mass spectrometry: corona discharge ion source for use in liquid chromatograph — mass spectrometer — computer analytical system, *Analyt. Chem.*, 47, 14, 2369–2373, 1975.
- Castleman, A. W., Jr., Clusters, *Env. Sci. Technol.*, 22, 1, 1265–1267, 1988.
- Cicerone, R. J., Shetter, J. D., Stedman, D. H., Kelly, T. J., and S. C. Liu, Atmospheric N₂O: measurements to determine its sources, sinks, and variations, *J. Geophys. Res.*, 83, C6, 3042–3050, 1978.
- Cicerone, R. J., and R. Zellner, The atmospheric chemistry of hydrogen cyanide (HCN), *J. Geophys. Res.*, 88, C15, 10689–10696, 1983.
- Cicerone, R. J., How has the atmospheric concentration of CO changed?, in *The Changing Atmosphere*, eds. F. S. Rowland and J. S. A. Isaksen, pp.49–61, 1988.

- Cohen, M. J., and F W Karasek, Plasma chromatography™ — a new dimension for gas chromatography and mass spectrometry, *J. Chromat. Sci.*, 8, 330–337, 1970.
- Colbeck, J., and Roy M. Harrison, The concentrations of specific C₂–C₆ hydrocarbons in the air of NW England, *Atm. Env.*, 19, 11, 1899–1904, 1985.
- Cronn, D. R., R. A. Rasmussen, E. Robinson, and D. E. Harsch, Halogenated compound identification and measurement in the troposphere and lower stratosphere, *J. Geophys. Res.*, 82, 37, 5935–5944, 1977.
- Cunnold, D. M., R. G. Prinn, R. A. Rasmussen, P. G. Simmonds, F. N. Alyea, A. A. Cardelino, A. J. Crawford, P. J. Fraser, and R. D. Rosen, Atmospheric lifetime and annual release estimates for CFC₁₃ and CF₂Cl₂ from 5 years of ALE data, *J. Geophys. Res.*, 91, D10, 10797–10817, 1986.
- Danilov, 1968: Данилов, А. Д. *Химия, атмосфера и космос*. Ленинград: Гидрометеониздат, 1968.
- Danilov and Vlassov, 1973: Данилов, А. Д. и М. Н. Власов, *Фотохимия ионизированных и возбужденных частиц в нижней ионосфере*. Ленинград: Гидрометеониздат. 1973.
- DeLorey, D. C., D. R. Cronn, and J. C. Farmer, Tropospheric latitudinal distributions of CF₂Cl₂, CFC₁₂, N₂O, CH₃CCl₃ and CCl₄ over the remote pacific ocean, *Atm. Env.*, 22, 7, 1481–1494, 1988.
- Donahue, Neil M., and Ronald G. Prinn, Nonmethane hydrocarbon chemistry in the remote marine boundary layer, *J. Reophys. Res.*, 95, D11, 18387–18411, 1990.
- Dunkin, D. B., F. C. Fehsenfeld, A. L. Schmeltekopf, and E. E. Ferguson, Ion-molecule reaction studies from 300° to 600°K in a temperature-controlled flowing afterglow system, *J. Chem. Phys.*, 49, 3, 1365–1371, 1968.
- Dzidic, J., D. J. Carroll, R. N. Stillwell., and E. C. Horning, Comparison of positive ions formed in Nickel 63 and corona discharge ion sources using nitrogen, argon, isobutane, ammonia and nitric oxide as reagents in atmospheric pressure ionization mass spectrometry, *Analyt. Chem.*, 48, 1763–1768, 1976.
- Eisele, F., Direct tropospheric ion sampling and mass identification, *Int. J. Mass Spectr. Ion Proc.*, 54, 119–126, 1983.
- Eisele, F. L., and E. W. McDaniel, Mass spectrometric study of tropospheric ions in the northeastern and southwestern United States, *J. Geophys. Res.*, 91, D4, 5183–5188, 1986.
- Eisele, F. L., Identification of tropospheric ions, *J. Geophys. Res.*, 91, D7, 7897–7906, 1986.
- Eisele, F. L., First tandem mass spectrometric measurement of tropospheric ions, *J. Geophys. Res.*, 93, D1, 716–724, 1988.
- Eisele, F. L., Natural and anthropogenic negative ions in the troposphere, *J. Geophys. Res.*, 94, D2, 2183–2196, 1989a.
- Eisele, F. L., Natural and transmission line produced positive ions, *J. Geophys. Res.*, 94, D5, 6309–6318, 1989b.
- Eisele, F. L., and D. J. Tanner, Identification of ions in continental air, *J. Geophys. Res.*, 95, D12, 20539–20550, 1990.
- Eisele, F. L., and D. J. Tanner, Ion-assisted tropospheric OH measurements, *J. Geophys. Res.*, 96, D5, 9295–9308, 1991.

- Eisele, F. L., and D. J. Tanner, Measurement of the gas phase concentration of H_2SO_4 and methane sulfonic acid and estimates of H_2SO_4 production and loss in the atmosphere, *J. Geophys. Res.*, **98**, D5, 9001–9010, 1993.
- Fabian, P., R. Borchers, B. C. Krüger, and S. Lal, CF_4 and C_2F_6 in the atmosphere, *J. Geophys. Res.*, **92**, D8, 9831–9835, 1987.
- Fehsenfeld, F. C., and E. E. Ferguson, The origin of water cluster ions in the D-region, *J. Geophys. Res.*, **74**, 2217, 1969.
- Fehsenfeld, F. C., C. J. Howard, and A. L. Schmeltekopf, Gas phase chemistry of HNO_3 , *J. Chem. Phys.*, **63**, 7, 2835–2841, 1975.
- Fehsenfeld, F. C., P. J. Crutzen, A. L. Schmeltekopf, Carleton J. Howard, D. L. Albritton, E. E. Ferguson, J. A. Davidson, and H. I. Schiff, Ion chemistry of chlorine compounds in the troposphere and stratosphere, *J. Geophys. Res.*, **81**, 24, 4454–4460, 1976.
- Ferguson, E. E., Rate constants of thermal energy binary ion-molecule reactions of aeronomic interest, *At. Data Nucl. Data Tables*, **12**, 159–178, 1973.
- Ferguson, E. E., and F. Arnold, Ion chemistry in the stratosphere, *Acc. Chem. Res.*, **14**, 11, 327–334, 1981.
- Fite, W. L., and J. A. Rutherford, Negative ions in afterglows in atmospheric gases, *Discuss. Faraday Soc.*, **37**, 192–202, 1964.
- Fishman, J., P. J. Crutzen, A numerical study of tropospheric photochemistry using a one-dimensional model, *J. Geophys. Res.*, **82**, 37, 5897–5906, 1977.
- Frank, H., W. Frank, and H. J. C. Neves, Airborne C_1 - and C_2 - halocarbons at four representative sites in Europe, *Atm. Env.*, **25A**, 2, 257–261, 1991.
- Fraser, P. J. B., and G. J. Pearman, Atmospheric halocarbons on the southern hemisphere, *Atm. Env.*, **12**, 839–844, 1978.
- Fraser, P. J., P. Hydsen, J. G. Enting, and G. J. Pearman, Global distribution and southern hemisphere trends of atmospheric CCl_3F , *Nature*, **302**, 5910, 692–695, 1983.
- Freeman, Gordon R., and David A. Armstrong, Electron and ion mobilities, *Adv. At. Mol. Phys.*, **20**, 267–325, 1985.
- Gear, C. W., The automatic integration of ordinary differential equations, *Comm. ACM*, **14**, 3, 176–179, 1971.
- Giles, K., and E. P. Grimsrud, The kinetic ion mobility mass spectrometry: measurements of ion-molecule reaction rate constants at atmospheric pressure, *J. Phys. Chem.*, **96**, 6680–6687, 1992.
- Golombek, Amram, and Ronald G. Prinn, A global three-dimensional model of the circulation and chemistry of CFCl_3 , CF_2Cl_2 , CH_3CCl_3 , CCl_4 , and N_2O , *J. Geophys. Res.*, **91**, D3, 3985–4001, 1986.
- Grennfelt, P., Investigation of gaseous nitrates in an urban and a rural area, *Atm. Env.*, **14**, 311–316, 1980.
- Gringel, W., Käselau, K. H., and R. Mühleisen, Recombination rates of small ions and their attachment to aerosol particles, *Pageoph*, **116**, 1101–1113, 1978.
- Grosjean, D., and F. Kochy, Hydrocarbons and carbonyls in Los Angeles air, *J. Air Pollut. Contr. Assoc.*, **34**, 5, 537–543, 1984.
- Grosjean, D., A. H. Miguel, and T. M. Tavares, Urban air pollution in Brazil: acetaldehyde and other carbonyls, *Atm. Env.*, **24B**, 1, 101–106, 1990.

- Harrison, Roy. M., and A. G. Allen, Measurements of atmospheric HNO_3 , HCl and associated species on a small network in Eastern England, *Atm. Env.*, 24A, 2, 369–376, 1990.
- Hayhurst, C. J., P. Watts, and A. Wilders, Studies on gas-phase ion/molecule reactions of relevance to ion mobility spectrometry: mass analysis and ion identification of the negative reactant ion peak in “clean” air, *Int. J. Mass Spectr. Ion Proc.*, 121, 127–139, 1992.
- Heidt, L. E., J. F. Vedder, W. H. Pollock, R. A. Lueb, and B. E. Henry, Trace gases in the Antarctic Atmosphere, *J. Geophys. Res.*, 94, D9, 11599–11611, 1989.
- Heikes, B. G., G. L. Kok, J. G. Walega, and A. L. Lazrus, H_2O_2 , O_3 and SO_2 measurements in the lower troposphere over the eastern United States during fall, *J. Geophys. Res.*, 92, D1, 915–931, 1987.
- Heitmann, H., and F. Arnold, Composition measurements of tropospheric ions, *Nature*, 306, 747–751, 1983.
- Hewitt, C. N., and R. M. Harrison, Tropospheric concentrations of the hydroxyl radical — a review, *Atm. Env.*, 19, 4, 545–554, 1985.
- Hierl, P. M., A. F. Ahrens, M. Henchman, A. A. Viggiano, and J. F. Paulson, Rate constants and product distributions as functions of temperature for the reaction of $\text{OH}^-(\text{H}_2\text{O})_{0,1,2}$ with CH_3CN , *Int. J. Mass Spectr. Ion Proc.*, 81, 101–122, 1987.
- Hiraoka, K., and P. Kebarle, Temperature dependence of third order ion molecule reactions. The reaction $\text{H}_3^+ + 2\text{H}_2 = \text{H}_5^+ + \text{H}_2$, *J. Chem. Phys.*, 63, 2, 746–749, 1975.
- Hiraoka, Kenzo, Temperature dependence of reactions of N_4^+ and N_3^+ with O_2 in the range 552–64K, *J. Chem. Phys.*, 91, 10, 6071–6076, 1989.
- Hough, Adrian M., Development of a two-dimensional global tropospheric model: model chemistry, *J. Geophys. Res.*, 96, D4, 7325–7362, 1991.
- Hov, Ø., S. A. Penkett, J. S. A. Isaksen, and A. Semb, Organic gases in the Norwegian Arctic, *Geophys. Res. Lett.*, 11, 5, 425–428, 1984.
- Hov, Ø., N. Schmidbauer, and M. Oehme, Light hydrocarbons in the Norwegian Arctic, *Atm. Env.*, 23, 11, 2471–2482, 1989.
- Huertas, M. L., Marty, A. M., and J. Fontan, On the nature of positive ions of tropospheric interest and on the effect of polluting organic vapors, *J. Geophys. Res.*, 79, 12, 1737–1743, 1974.
- Huertas, M. L., and J. Fontan, Evolution times of tropospheric positive ions, *Atm. Env.*, 9, 1018–1026, 1975.
- Huertas, M. L., J. Fontan, and J. Gonzalez, Evolution times of tropospheric negative ions, *Atm. Env.*, 12, 2351–2362, 1978.
- Huertas, M. L., and J. Fontan, Formation of stable positive and negative ions of tropospheric interest, *Atm. Env.*, 16, 10, 2521–2527, 1982.
- Hübler, G., D. Perner, U. Platt, A. Tönnissen, and D. H. Ehhalt, Groundlevel OH measurements by optical absorption, *J. Geophys. Res.*, 89, D1, 1309–1319, 1984.
- Iher and Salm, 1981: Ихер, X. P. и Я. Сальм, Зависимость спектра подвижности легких аэрионов от их возраста. *Acta Comm. Univ. Tartuensis*, 588, 33–39, 1981.
- Iher and Salm, 1982: Ихер, X. P. и Я. Сальм, Зависимость спектра подвижности легких аэрионов от химических примесей в воздухе. *Acta Comm. Univ. Tartuensis*, 631, 27–34, 1982.

- Ikezoe, Y., S. Matsuoka, M. Takebe, and A. A. Viggiano, Gas phase ion molecule reaction rate constants through 1986, *Maruzen Co. Tokyo, Japan: Ion Research group of the Mass Spectrometry Society of Japan*, 1987.
- Isaksen, Ivar S. A., and Ø. Hov, Calculation of trends in the tropospheric concentration of O₃, OH, CO, CH₄ and NO_x, *Tellus*, 39B, 271–285, 1987.
- Israël, H., *Atmospheric electricity (volume I)*, Keter Press, Jerusalem, 1970.
- Jacob, P., T. M. Tavares, V. C. Rocha, and D. Klockow, Atmospheric H₂O₂ field measurements in a typical environment: Bahia, Brazil, *Atm. Env.*, 24A, 2, 377–382, 1990.
- Jennings, K. R., Recent developments in the study of ion-molecule reactions, *Adv. Mass Spectr.*, 7A, 209–228, 1978.
- Johnsen, R., Temperature dependence of association of diatomic ions in diatomic gases, *J. Chem. Phys.*, 85, 7, 3869–3873, 1986.
- Jones, B. M. R., R. A. Cox, and S. A. Penkett, Atmospheric chemistry of carbon disulphide, *J. Atmos. Chem.*, 1, 65–86, 1983.
- Junge, 1965: Юнге, X. *Химический состав и радиоактивность атмосферы*. Москва: Мир, 1965.
- Juuti, S., J. Arey, and R. Atkinson, Monoterpene emission rate measurements from a monterey pine, *J. Geophys. Res.*, 95, D6, 7515–7519, 1990.
- Karasek, F. W., Plasma chromatography, *Analyt. Chem.*, 46, 710–720, 1974.
- Karol *et al.*, 1983: Кароль, И. Л., В. В. Розанов, и Ю. М. Тимофеев, *Газовые примеси в атмосфере*. Ленинград: Гидрометеоиздат, 1983.
- Kawamoto, H., and T. Ogawa, A steady state model of negative ions in the lower stratosphere, *Planet. Space Sci.*, 32, 10, 1223–1233, 1984.
- Kawamoto, H., and T. Ogawa, First model of negative ion composition in the troposphere, *Planet. Space Sci.*, 34, 12, 1229–1239, 1986.
- Khan, A., Theoretical studies of the clathrate structures of (H₂O)₂₀, H⁺(H₂O)₂₀ and H⁺(H₂O)₂₁, *Chem. Phys. Lett.*, 217, 4, 443–450, 1994.
- Keesee, R. G., and A. W. Castleman, Jr., The chemical kinetics of aerosol formation, In *Topics in Current Physics, Vol. 28: The Stratospheric Aerosol Layer*, ed. R. C. Whitten, Springer-Verlag, Berlin, 69–92, 1982.
- Keesee, R. G., and A. W. Castleman, Jr., Understanding the middle atmosphere via laboratory: ion cluster investigations, *Ann. Geophys.*, 1, 1, 75–80, 1983.
- Keesee, R. G., and A. W. Castleman, Jr., Ions and cluster ions: experimental studies and atmospheric observations, *J. Geophys. Res.*, 90, D4, 5885–5890, 1985.
- Keesee, R. G., and A. W. Castleman, Jr., Thermochemical data on gas-phase ion-molecule association and clustering reactions, *J. Phys. Chem. Ref. Data*, 15, 3, 1011–1071, 1986.
- Kelly, Thomas J., R. Mukund, Chester W. Spicer, and Albert J. Pollack, Concentrations and transformations of hazardous air pollutants, *Environ. Sci. Technol.*, 28, 8, 378–387, 1994.
- Kikas, Ü., A. Mirme and E. Tamm, Size distribution dynamics of rural and urban aerosols, *Acta Comm. Univ. Tartuensis*, 880, 84–93, 1990.
- Kikas, Ü., V. Kimmel, and A. Mirme, Spectra of near-ground atmospheric aerosols, *Acta Comm. Univ. Tartuensis*, 947, 125–135, 1992.
- Kilpatrick, W. D., An experimental mass-mobility relation for ions in air at atmospheric pressure, *Proc. Annu. 19. th. Conf. Mass Spectrosc.*, 320–325, 1971.

- Kim, S. H., F. W. Karasek, and S. Rokushika, Plasma chromatography with ammonium reactant ions, *Anal. Chem.*, 50, 1, 152–155, 1978.
- Kleinman Lawrence J., Photochemical formation of peroxides in the boundary layer, *J. Geophys. Res.*, 91, D10, 10889–10904, 1986.
- Кноп, G., and F. Arnold, Nitric acid vapour measurements in the troposphere and lower stratosphere by chemical ionization mass spectrometry, *Planet. Space Sci.*, 33, 8, 983–986, 1985.
- Kochanski, E., Theoretical studies of the system $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ for $n = 1-9$, *J. Am. Chem. Soc.*, 107, 7869–7873, 1985.
- Kolokolov *et al.*, 1980: Колоколов, В. П., А. М. Скоробогатова и М. М. Харлова, Концентрация легких аэрионов в курортной зоне Ленинграда, *Труды Гл. Геофиз. Обсерв.*, 401, 126–129 1980.
- Koropalov, 1988: Коропалов, В. М. Малые газовые примеси в атмосфере над океаном, *ФАО*, 24, 8, 835–843, 1988.
- Кнопте *et al.*, 1990: Кнопте, Д. Г., Л. Ф. Крылова и В. С. Музыкантов, *Физическая химия*. Москва: Высшая школа, 1990.
- Krey, P. W., R. J. Lagomarsino, and L. E. Toonkel, Gaseous halogens in the atmosphere in 1975, *J. Geophys. Res.*, 82, 12, 1753, 1977.
- Kuttler, W., Spurenstoffe in the Atmosphäre, *Geoökodynamik*, 5, 29–76, 1984.
- Lau, Y. K., S. Ikuta, and P. Kebarle, Thermodynamics and kinetics of the gas-phase reactions: $\text{H}_3\text{O}^+(\text{H}_2\text{O})_{n-1} + \text{H}_2\text{O} = \text{H}_3\text{O}^+(\text{H}_2\text{O})_n$, *J. Am. Chem. Soc.*, 104, 1462–1469, 1982.
- Lawless, P. A., and L. E. Sparks, Measurement of ion mobilities in air and sulfur dioxide-air mixtures as a function of temperature, *Atm. Env.*, 14, 481, 1980.
- Lee, H. S., and R. Johnsen, Ion-ion recombination studies in ambient helium and argon at atmospheric densities, *J. Chem. Phys.*, 90, 11, 6328–6334, 1989.
- Leinster, P., R. Perry, and R. J. Young, Ethylene dibromide in the urban air, *Atm. Env.*, 12, 2383–2387, 1978.
- Leite, 1980: Лейте, В. *Определение загрязнений воздуха в атмосфере и на рабочем месте*. Ленинград: Химия, 1980.
- Lifshitz *et al.*, 1983: Лившиц, А. И., Ф. Г. Портнов и А. Б. Шмидт, Моделирование химической кинетики образования отрицательных ионов в воздухе с нулевой влажностью. *Изв. АН Латв. ССР, сер. хим.*, 4, 449–451, 1983.
- Lifshitz *et al.*, 1984: Лившиц, А. И., Ф. Г. Портнов и А. В. Шмидт, Влияние влажности на химический состав ионов в воздухе. *Изв. АН Латв. ССР, сер. хим.*, 2, 192–196, 1984.
- Levin, M., and S. Ulm, *Arvutusmeetodite käsiraamat*, Tallinn, Valgus, 1966.
- Lightman, P., A. S. Kallend, A. R. W. Marsh, B. M. R. Jones, and S. A. Penkett, Seasonal variation of hydrocarbons in the free troposphere at mid-latitudes, *Tellus*, 42B, 408–422, 1990.
- Lindinger, W., M. McFarland, F. C. Fehsenfeld, D. L. Albritton, A. L. Schmeltekopf, and E. E. Ferguson, Translation and internal energy dependences of some ion-neutral reactions, *J. Chem. Phys.*, 63, 5, 2175–2181, 1975.
- Lowe David C., and Schmidt Ulrich, Formaldehyde (HCHO) measurements in the nonurban atmosphere, *J. Geophys. Res.*, 88, C15, 10844–10858, 1983.

- Luts, A., Evolution of small ions at enhanced ionization, in *Proc. 9th Int. Conf. on Atmospheric Electricity*, pp. 532–535, St. Petersburg, 1992a.
- Luts, A., Chemical kinetics of tropospheric ions at higher ionization rates, *Acta Comm. Univ. Tartuensis*, 950, 39–57, 1992b.
- Luts, A., Evolution of negative small ions at enhanced ionization, *J. Geophys. Res.*, 100, 1487–1496, 1995.
- Luts, A., and J. Salm, Modeling of the evolution of small tropospheric ions, *Acta Comm. Univ. Tartuensis*, 947, 5–23, 1992a.
- Luts, A., and J. Salm, Chemical Composition of Small Air Ions in Near-Ground Layer, in *Proc. 9th Int. Conf. on Atmospheric Electricity*, pp.75–77, St. Petersburg, 1992b.
- Luts, A., and J. Salm, Chemical composition of small atmospheric ions near the ground, *J. Geophys. Res.*, 99, 10781–10785, 1994.
- Matsuoka, Shingo, and Hirone Nakamura, Pressure and temperature dependences of the “binary” ion-molecule reaction $N_3^+ + H_2O \rightarrow H_2NO^+ + N_2$, *J. Chem. Phys.*, 89, 9, 5663–5669, 1988.
- McDaniel, E. W., and E. A. Mason, *The mobility and diffusion of ions in gases*, John Wiley and Sons, New York – London – Sydney – Toronto, 1973.
- McFarland, M., D. L. Albritton, F. C. Fehsenfeld, E. E. Ferguson, and A. L. Schmeltekopf, Flow-drift technique for ion mobility and ion-molecule reaction rate constant measurements. I. Apparatus and mobility measurements, *J. Chem. Phys.*, 59, 12, 6610–6619, 1973a.
- McFarland, M., D. L. Albritton, F. C. Fehsenfeld, E. E. Ferguson, and A. L. Schmeltekopf, Flow-drift technique for ion mobility and ion-molecule reaction rate constant measurements. II. Positive ion reactions of N^+ , O^+ , and N_2^+ with O_2 and O^+ with N_2 from thermal to $\sim 2eV$, *J. Chem. Phys.*, 59, 12, 6620–6628, 1973b.
- McFarland, M., D. L. Albritton, F. C. Fehsenfeld, E. E. Ferguson, and A. L. Schmeltekopf, Flow-drift technique for ion mobility and ion-molecule reaction rate constant measurements. III. Negative ion reactions of O^- with CO , NO , H_2 , and D_2 , *J. Chem. Phys.*, 59, 12, 6629–6635, 1973c.
- Meisels, G. G., F. Botz, R. K. Mitchum, and E. F. Heckel, Angular momentum and the temperature-dependence of ion-molecule reactions, *Adv. Mass Spectr.*, 7A, 250–257, 1978.
- Meot-Ner, M., and F. H. Field, Correlations between rate, temperature dependence, exothermicity, and reactant structure in slow ion-molecule reactions, *Adv. Mass Spectr.*, 7A, 117–124, 1978.
- Meyerott, R. E., J. B. Reagan, and R. G. Joiner, The mobility and concentration of ions and the ionic conductivity in the lower stratosphere, *J. Geophys. Res.*, 85, A3, 1273–1278, 1980.
- Michio, Hirota, and Muramatsu Hisafumi, Gas-chromatographic measurements of atmospheric sulfur hexafluoride, *Bull. Chem. Soc. Jap.*, 59, 1, 329–331, 1986.
- Miller, T. M., R. E. Wetterskog, and J. F. Paulson, Temperature dependence of the ion-molecule reactions $N^+ + CO$, $C^+ + NO$, and $C^+ + CO_2$ from 90–450K, *J. Chem. Phys.*, 80, 10, 4922–4925, 1984.
- Misaki, M., Studies on the atmospheric ion spectrum, *Pap. Met. Geophys.*, 12, 3/4, 247–270, 1961.
- Mitra, A. P., Atmospheric chemistry, *Indian J. Radio Space Phys.*, 19, 383–399, 1990.

- Mohan Rao, A. M., and Gauri G. Pandit, Concentrations of C₂-C₅ hydrocarbons in atmospheric air at Deonar, Bombay in relation to possible sources, *Atm. Env.*, 22, 2, 395-401, 1988.
- Mohnen, V. A., Discussion of the formation of major positive and negative ions up to the 50 km level, *Pure Appl. Geophys.*, 84, 141, 1971.
- Mohnen, V. A., Negative ions in air-like gas mixtures, *Pure Appl. Geophys.*, 100, 123-132, 1972.
- Mohnen, V. A., Formation, nature and mobility of ions of atmospheric importance, in *Electrical Processes in Atmospheres*, Darmstadt, D. Steinkopf Verlag, 1-17, 1977.
- Mohnen, V. A., J. Del Santo, and J. A. Kadlecik, Nature, mobility and physico-chemical reactivity of ions in the lower atmosphere (<40 km), *Proc. 6th. Int. Conf. Atmos. Electricity, Manchester*, 28. July-1. Aug., 1980.
- Mohnen, V. A., Stratospheric ion and aerosol chemistry and possible links with cirrus cloud microphysics—a critical assessment, *J. Atm. Sci.*, 47, 16, 1933-1948, 1990.
- Mowrer, Jacques, and Anne Lindskog, Automatic unattended sampling and analysis of background levels of C₂-C₅ hydrocarbons, *Atm. Env.*, 25A, 9, 1971-1979, 1991.
- Nagato, K., and T. Ogawa, Atmospheric ion mobility spectra near the ground, *Planet. Space Sci.*, 36, 2, 163-176, 1988.
- Narcisi, R. S., Ion composition measurements and related ionospheric processes in the D and lower E regions, *Ann. Geophys.*, 22, 2, 224-234, 1966.
- Noxon, J. F., Norton, R. B., and E. Marovich, NO₃ in the troposphere, *Geophys. Res. Lett.*, 7, 2, 125-128, 1980.
- Parts, 1988: Партс, Т. М. О природе положительных легких аэрионов однокундного возраста, *Acta Comm. Univ. Tartuensis*, 824, 69-77, 1988.
- Parts, T., and J. Salm, The effect of pyridine and its homologues on mobility spectra of positive small air ions, *Acta Comm. Univ. Tartuensis*, 947, 24-30, 1992.
- Parts, T., The effect of some alkylamines on mobility spectra of small air ions, *Acta Comm. Univ. Tartuensis*, 950, 59-65, 1992.
- Peifer, W. R., M. T. Coolbaugh, and J. F. Garvey, Observation of "magic numbers" in the population distributions of the (NH₃)_{n-1}NH₂⁺ and (NH₃)_nH₂⁺ cluster ions: implications for cluster ion structures, *J. Chem. Phys.*, 91, 11, 6684-6690, 1989.
- Perkins, M. D., and F. L. Eisele, First mass spectrometric measurements of atmospheric ions at ground level, *J. Geophys. Res.*, 89, D6, 9649-9657, 1984.
- Pfeilsticker, K., and F. Arnold, First ion composition measurement in the stratopause region, using a rocket-borne parachute drop sonde, *Planet. Space Sci.*, 37, 3, 315-328, 1989.
- Platt, U. F., A. M. Winer, H. W. Biermann, R. Atkinson, and J. N. Pitts, Jr., Measurement of nitrate radical concentrations in continental air, *Envir. Sci. Technol.*, 18, 365-369, 1984.
- Poltorak, 1991: Полтора́к, О. М. *Термодинамика в физической химии*. Москва: Высшая школа, 1991.
- Puxbaum, H., C. Rosenberg, M. Gregori, C. Lanzerstorfer, E. Ober, and W. Winiwarter, Atmospheric concentrations of formic and acetic acid and related compounds in eastern and northern Austria, *Atm. Env.*, 22, 12, 2841-2850, 1988.
- Rakitski *et al.*, 1979: РАКИТСКИЙ, Ю. В., С. М. УСТИНОВ и И. Г. ЧЕРНОРУЦКИЙ, *Численные методы решения жестких систем*. Москва: Наука, 1979.

- Rakitski *et al.*, 1982: Ракитский, Ю. В., С. М. Устинов, Ю. Б. Сениченков и С. И. Воскобойников, *Алгоритмы и программы интегрирования дифференциальных уравнений*. Ленинград, Ленинградский политехнический институт, 1982.
- Rasmussen, R. A., M. A. K. Khalil, and R. J. Fox, Altitudinal and temporal variation of hydrocarbons and other gaseous tracers of arctic haze, *Geophys. Res. Lett.*, 10, 2, 144–147, 1983.
- Rasul, 1976: Расул, С. (ред.). *Химия нижней атмосферы*. Москва, 1976.
- Retalis Dimitris, A., On the relationship between small atmospheric ions concentration and (1) smoke, (2) sulfur dioxide and (3) wind speed, *Pure Appl. Geophys.*, 115, 3, 575–581, 1977.
- Riba, M. L., J. P. Tathy, N. Tsiropoulos, B. Monsarrat, and L. Torres, Diurnal variation in the concentration of α -pinene and β -pinene in the Landes Forest (France), *Atm. Env.*, 21, 1, 191–193, 1987.
- Rudolph, J., D. H. Ehhalt, A. Khedim, Vertical profiles of acetylene in the troposphere and stratosphere, *J. Atmos. Chem.*, 2, 2, 117–124, 1984a.
- Rudolph, J., C. Jebsen, A. Khedim, and F. J. Johnen, Measurements of the latitudinal distribution of light hydrocarbons and halocarbons over the Atlantic, *Phys. -Chem. Behav. Atmos. Pollut. Proc. 3 Eur. Symp., Varese, 10. -12. Apr. 1984*, 492–501, 1984b.
- Salm and Matisen, 1977: Сальм, Я. и Р. Л. Матизен, Некоторые результаты исследования влияния примесей воздуха на спектр подвижности легких отрицательных аэрионов, *Acta Comm. Univ. Tartuensis*, 443, 40–43, 1977.
- Salm and Iher, 1983: Сальм, Я. Й. и Х. Р. Ихер, Исследование спектра подвижности легких аэрионов. *Труды ИЭМ*, 30(104), 116–121, 1983.
- Salm, 1987: Сальм, Я. Соединение аэрионов при симметричной стационарной ионизации. *Acta Comm. Univ. Tartuensis*, 755, 10–16, 1987.
- Salm and Luts, 1988: Сальм, Я. и А. Лутс, Метод вычисления стационарных концентраций одного класса задач химической кинетики. *Acta Comm. Univ. Tartuensis*, 824, 52–59, 1988.
- Salm, 1992: Сальм, Я. Зависимость подвижности иона от его массы. *Acta Comm. Univ. Tartuensis*, 950, 66–72, 1992.
- Salm, J., H. Tammet, H. Iher, and U. Hõrrak, The dependence of small air ion mobility spectra in the ground layer of the atmosphere on temperature and pressure, *Acta Comm. Univ. Tartuensis*, 947, 50–56, 1992.
- Salm, 1993: Сальм, Я. Ионы в приземном слое атмосферы, *Химия плазмы*, 194–217. Москва: Энергоатомиздат, 1993.
- Sampath, S., V. Sasikumar, and S. Muralidas, Positive and negative ion densities and mobilities in the middle atmosphere over India — rocket measurements, *J. Atm. Terr. Phys.*, 54, 3/4, 347–354, 1992.
- Schlager, H., and F. Arnold, Implications for atmospheric negative ion composition measurements of laboratory ECA studies of sulfuric acid cluster ions, *Planet. Space Sci.*, 34, 2, 245–252, 1986.
- Schmidt, U., The latitudinal and vertical distribution of molecular hydrogen in the troposphere, *J. Geophys. Res.*, 83, C2, 941–946, 1978.

- Schofield, K., Evaluated chemical kinetic rate constants for various gas phase reactions, *J. Phys. Chem. Ref. Data*, 2, 1, 1973.
- Sheppard, J. C., R. J. Hardy, and J. F. Hopper, Antarctic hydroxyl radical measurements, *Antarct. J. US.*, 18, 5, 243–244, 1983.
- Siegel, M. W., and W. L. Fite, Terminal ions in weak atmospheric pressure plasmas. Applications of atmospheric pressure ionization to trace impurity analysis in gases, *J. Phys. Chem.*, 80, 2871–2881, 1976.
- Sild and Palm, 1986: Силд, В. А. и В. А. Пальм, Реализация универсального алгоритма решения прямых задач для гомогенных равновесно-кинетических систем, *Реакционная способность органических соединений*, 23, 4(84), 483–507, 1986.
- Singh, Hanwant B., Louis J. Salas, Bruce K. Cantrell, and Robin M. Redmond, Distribution of aromatic hydrocarbons in the ambient air, *Atm. Env.*, 19, 1911–1919, 1985.
- Sjödin, Å., and M. Ferm, Measurements of nitrous acid in an urban area, *Atm. Env.*, 19, 6, 985–992, 1985.
- Smirnov, 1980: Смирнов, В. В. Атмосферные ионы, *Труды ИЭМ*, 24(89), 3–28 1980.
- Smith, S. C., M. J. McEwan, and R. G. Gilbert, The pressure dependence of ion-molecule association rate coefficients, *J. Chem. Phys.*, 90, 3, 1630–1640, 1989.
- Solomon, S., R. W. Sanders, G. H. Mount, M. A. Carroll, R. O. Jakoubek, and A. L. Schmeltekopf, Atmospheric NO₃. Observations in polar regions, *J. Geophys. Res.*, 94, D13, 16423–16427, 1989.
- Sze, Nien Dak, and K. W. Co. Malcolm, Photochemistry of COS, CS₂, CH₃SCH₃ and H₂S: implications for the atmospheric sulfur cycle, *Atm. Env.*, 14, 1223–1239, 1980.
- Stephens Edgar R., Tropospheric methane concentrations between 1963 and 1970, *J. Geophys. Res.*, 90, D7, 13076–13080, 1985.
- Takebe, M., Positive ion species and their mobilities in air, *Jap. J. Appl. Phys.*, 13, 2, 207–217, 1974.
- Talbot, R. W., A. S. Vijgen, and R. C. Harriss, Measuring of tropospheric HNO₃: problems and prospects for nylon filter and mist chamber techniques, *J. Geophys. Res.*, 95, D6, 7553–7561, 1990.
- Таммет, 1975: Таммет, Х. Ф. Зависимость спектра подвижностей легких аэрионов от микропримесей воздуха, *Acta Comm. Univ. Tartuensis*, 348, 3–15, 1975.
- Таммет, Н., Н. Iher, and J. Salm, Spectrum of atmospheric ions in the mobility range 0,32 cm²/(V·s) – 3,2 cm²/(V·s), *Acta Comm. Univ. Tartuensis*, 947, 35–49, 1992.
- Таммет, Н., Size-mobility relation for ultrafine particles, In *European Aerosol Conference, Single Page Abstracts*, 139, Oxford, 1992.
- Таммет, Н., Size and mobility of nanometer particles, clusters and ions, *J. Aerosol Sci.*, 26, 3, 459–476, 1995.
- Tanner, D. J., and F. L. Eisele, Ions in oceanic and continental air masses, *J. Geophys. Res.*, 96, D1, 1023–1031, 1991.
- Thomas, L., Modelling of the ion composition of the middle atmosphere, *Ann. Geophys.*, 1, 1, 61–73, 1983.

- Tille, K. J. W., M. Savelsberg, and K. Bächmann, Airborne measurements of non-methane hydrocarbons over Western Europe: vertical distributions, seasonal cycles of mixing ratios and source strengths, *Atm. Env.*, 19, 11, 1751–1760, 1985.
- Turco, R. P., P. Hamill, O. B. Toon, R. C. Whitten, and C. S. Kiang, A one-dimensional model describing aerosol formation and evolution in the stratosphere: Physical processes and mathematical analogs, *J. Atmos. Sci.*, 36, 699–717, 1979.
- Tverskoi, 1962: Тверской, П. Н. *Курс метеорологии (атмосферная физика)*, Ленинград, 1962.
- Van Neste, A., Robert. A. Duce, and Cindy Lee, Methylamines in the marine troposphere, *Geophys. Res. Lett.*, 14, 7, 711–714, 1987.
- Vierkorn-Rudolph B., K. Bächmann, B. Schwarz, and F. X. Meixner, Vertical profiles of hydrogen chloride in the troposphere, *J. Atm. Chem.*, 2, 1, 47–63, 1984.
- Viggiano, A. A., R. A. Perry, D. L. Albritton, E. E. Ferguson, and F. C. Fehsenfeld, The role of H_2SO_4 in stratospheric negative-ion chemistry, *J. Geophys. Res.*, 85, C8, 4551–4555, 1980.
- Viggiano, A. A., R. A. Perry, D. L. Albritton, E. E. Ferguson, and F. C. Fehsenfeld, Stratospheric negative ion reaction rates with H_2SO_4 , *J. Geophys. Res.*, 87, 7340–7342, 1982.
- Viggiano, A. A., and J. F. Paulson, Temperature dependence of associative detachment reactions, *J. Chem. Phys.*, 79, 5, 2241–2245, 1983.
- Viggiano, A. A., F. Dale, and J. F. Paulson, Measurements of some stratospheric ion-molecule association rates: implications for ion chemistry and derived HNO_3 concentrations in the stratosphere, *J. Geophys. Res.*, 90, D5, 7977–7984, 1985.
- Viggiano, A. A., The temperature dependence of ion-molecule association rate coefficients in the low pressure limit, *J. Chem. Phys.*, 84, 1, 244–249, 1986.
- Viggiano, A. A., F. Dale, and John F. Paulson, Proton transfer reactions of $\text{H}^+(\text{H}_2\text{O})_{n=2-11}$ with methanol, ammonia, pyridine, acetonitrile, and acetone, *J. Chem. Phys.*, 88, 4, 2469–2477, 1988a.
- Viggiano, A. A., R. A. Morris, F. Dale, and J. F. Paulson, Tropospheric reactions of $\text{H}^+(\text{NH}_3)_m(\text{H}_2\text{O})_n$ with pyridine and picoline, *J. Geophys. Res.*, 93, D8, 9534–9538, 1988b.
- Viggiano, A. A., R. A. Morris, and J. F. Paulson, Temperature dependences of rate constants for reactions of CO_4^- with NO and SO_2 , *J. Chem. Phys.*, 91, 9, 5855–5856, 1989.
- Virin *et al.*, 1979: Вирин, Л. Н., Р. В. Джагацпаян, В. К. Карачевцев, В. К. Потапов и В. Л. Тальрозе, *Ионно-молекулярные реакции в газах*. Москва: Наука, 1979.
- Watts, P., and A. Wilders, On the resolution obtainable in practical ion mobility systems, *Int. J. Mass Spectr. Ion Proc.*, 112, 179–190, 1992.
- Watts, P., Studies on gas-phase ion/molecule reactions of relevance to ion mobility spectrometry: kinetic modelling of the reactions occurring in “clean” air, *Int. J. Mass Spectr. Ion Proc.*, 121, 141–158, 1992.
- Wei, S., Z. Shi, and A. W. Castleman, Jr., Mixed cluster ions as a structure probe: experimental evidence for clathrate structure of $(\text{H}_2\text{O})_{20}\text{H}^+$ and $(\text{H}_2\text{O})_{21}\text{H}^+$, *J. Chem. Phys.*, 94, 4, 3268–3270, 1991.
- Whitby, R. A., and P. E. Coffey, Measurement of terpenes and other organics in Adirondack Mountain pine forest, *J. Geophys. Res.*, 82, 37, 5928, 1977.

- Whitby, R. A., and E. R. Altwicker, Acetylene in the atmosphere: sources, representative ambient concentrations and ratios to other hydrocarbons, *Atm. Env.*, *12*, 1289–1296, 1978.
- Wisemberg, J., and G. Kockarts, Negative ion chemistry in the terrestrial D region and signal flow graph theory, *J. Geophys. Res.*, *85*, 4642–4652, 1980.
- Zafiriou, O. C., Alford, J., Herrera, M., Peltzer, E. T., and R. B. Gagosian, Formaldehyde in remote marine air and rain: flux measurements and estimates, *Geophys. Res. Lett.*, *7*, 5, 341–344, 1980.
- Ziereis, H., and F. Arnold, Gaseous ammonia and ammonium ions in the free troposphere, *Nature*, *321*, 503–505, 1986.

AEROIOONIDE EVOLUTSIOONI MATEMAATILINE MODELLEERIMINE

KOKKUVÕTE

Käesolevas töös on tegeldud õhus leiduvate kergete ionide moodustumise matemaatilise modelleerimise probleemidega.

Esimeses peatükis on antud ülevaade ülesande matemaatilist külge puudutavatest probleemidest ja nende probleemide lahendusvõimalustest. Selgub, et ionide moodustumist kirjeldava mudeli lahendamine on üpris komplitseeritud, seda isegi siis, kui järgida antud probleemi käsitlemisel tavaliselt alati tehtavaid lihtsustusi (põhiline lihtsustus: mudelis esinevate neutraalsete ainete kontsentratsioone käsitletakse muutumatutena, mis viib võrrandsüsteemi lineaarseks). Komplikatsioonid on tingitud sellest, et vastav võrrandsüsteem on suur (võrrandite arvuga üle 100) ja jäik (võrrandites esinevate liikmete suurusjärgud erinevad kuni 10^{12} korda). Vastava ülesande paremaks lahendamiseks on välja töötatud senistest efektiivsem lahendusmeetod, milline võimaldab rahuldava ajakuluga modelleerida nii ionkoostise ajalist muutumist kui ka statsionaarset ionkoostist. Lisaks on analüüsitud andmeid, millised on vajalikud ionide tekkimist ja rekombinatsiooni kirjeldavate suuruste korrektseks määramiseks.

Teises peatükis on analüüsitud ionide evolutsiooni kohta teada olevaid füüsikalisi-keemilisi andmeid: teadaolevaid mudeleid, erinevates tingimustes saadud mõõtmistulemusi ionkoostise kohta, mõõtmistulemusi ionkoostise muutumist tingivate faktorite kohta ja ionide moodustumist määravate reaktsioonide karakteristikuid. Analüüsi tulemusel võib öelda, et õhu tegelik ionkoostis on vägagi muutlik, kusjuures märkimisväärne osa õhus esinevatest ionidest on siimaani identifitseerimata. Siiski on teada mõned ionid, millised esinevad kõige sagedamini: positiivsetest ionidest püridiini sisaldavad ionid ja ionid $\text{NH}_4^+(\text{H}_2\text{O})_k(\text{NH}_3)_n$, negatiivsetest ionidest ionid $\text{NO}_3^-(\text{HNO}_3)_n(\text{H}_2\text{O})_m$ ja ionid $\text{HSO}_4^- \cdot \text{X} \cdot \text{Y}$. Ionkoostis sõltub väga tugevasti mitmete neutraalsete gaaside kontsentratsioonidest, nagu näiteks mitmed halogeenid, NO_2 , SO_2 , klooraadikhape, mitmed amiinid, atsetoon, triklooretüleen, dimetüülsulfoksiid, atsetonitriil ja püridiin. Suur osa teises peatükis käsitletavatest andmetest pärineb mitte mass-spektromeetriast, vaid liikuvusspektromeetriast, mistõttu on antud ülevaade ka liikuvusspektrite interpreteerimise probleemidest.

Analüüsitud on ioone moodustavate reaktsioonide kiiruste sõltuvust rõhust ja temperatuurist. Selgub, et mõlemad sõltuvused on tegelikult väga individuaalsed, kusjuures sõltuvuse konkreetne kuju pole tavaliselt teada, mistõttu käesolevas mudelis arvestatakse nimetatud sõltuvuste mõju vaid teatavatel erijuhtumitel. Temperatuurisõltuvust arvestatakse klasteri-

seerumisreaktsioonide juures, samal ajal jäetakse see sõltuvus arvestamata enamiku teist järku reaktsioonide juures, kuna viimatinimetatud reaktsioonide sõltuvus temperatuurist on üldjuhul palju nõrgem. Reaktsioonide kiiruste sõltuvust rõhust arvestatakse mudelis põhiliselt reaktsioonide tasakaalu-konstantide väärtuste ja keskkonna tiheduse muutumise kaudu.

Kolmandas peatükis on antud ülevaade teadaolevatest andmetest neutraalsete gaaside kontsentratsioonide kohta. Selgub, et mitmete teadaolevalt oluliste gaaside tegelikud kontsentratsioonid on küllaltki halvasti teada, mis tähendab ühtlasi, et nende gaasidega seotud mudeli osad on paratamatult määratud küllaltki ebatäpselt.

Esimeses kuni kolmandas peatükis esitatud analüüsi kokkuvõttes võib öelda, et algandmete praeguse taseme juures ei ole ionide evolutsiooni väga täpne modelleerimine sisuliselt võimalik, mistõttu tuleb pidada tehtud lihtsustusi mitte ainult paratamatuteks, vaid ka mõistlikeks.

Neljandas peatükis on antud lühiülevaade koostatud mudeli abil saadud põhilistest tulemustest ja põhilistest probleemidest; piirdutud on lühiülevaatega, kuna oluline osa saadud tulemustest on juba publitseeritud. Koostatud mudel sisaldab 207 positiivsetiooni, 151 negatiivsetiooni, 150 neutraalset gaasi ja 1605 ionmolekulaarreaktsiooni. Koostatud mudel on täiuslikum kui teadaolevates töödes esitatud teised mudelid: 1) Kui teised mudelid on uurinud ionkoostist vaid mingites konkreetsetes vanuses, siis käesolevas töös on modelleeritud ionkoostist peaaegu kogu ionide eluea jooksul, 2) Käesolevas töös saadud tulemused on vähemalt kvalitatiivses kooskõlas nii noorte ionide, umbes 1 s vanuste ionide kui ka statsionaarse ionkoostise kohta teada olevate katseandmetega, samal ajal pole teada ühtki teist mudelit, mis oleks sedavõrd heas kooskõlas kõigi eelpoolnimetatud katseandmetega, 3) Kuna käesolevas töös uuritakse ionkoostist peaaegu kogu ionide eluea jooksul, siis on võimalik modelleerida ka mitmeid täiendavaid teadaolevaid efekte, eriti neid, millised esinevad umbes 1 s vanuses, ühtlasi on selle kaudu võimalik märgata ning parandada mudeli mõningaid puudusi. Mis puutub teistesse töödesse, siis nimetatud efekte pole modelleeritud ja mitmed mudelites tegelikult esinevad puudused on jäänud märkamata.

Kokkuvõttes võib öelda, et eelpooltoodud analüüsi alusel koostatud mudel kirjeldab kerge aeroionide moodustumise põhiprotsessi üldjoontes õigesti, mis võimaldab uute andmete saamisel mudelit üpris hõlpsasti kaasajastada.

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