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Mathematical modelling in problems of the chemistry of the atmosphere

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ABSTRACT. The characteristics of the mathematical modelling of chemical processes in the atmosphere, their relationship with geophysical processes, their classification in terms of space-time scales, and the sensitivity of the models are examined. The possibilities of modelling the photochemical mechanisms of the reactions of oxygen-, hydrogen-, nitrogen-, sulphur-, and carbon-containing compounds in the background atmosphere and in air in polluted regions and the selection of the parametrisation conditions in conformity with the aims of the given tasks and the hydrometeorological regime are analysed.

The experience gained in the practical use of models of the quality of air in designing a monitoring strategy and measures for the protection of nature is surveyed.

The bibliography includes 133 references.

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I. Introduction

Phenomena such as climate warming, the change in the ozone layer, acid rain, the inhibition of plant growth and destruction of forests, and smog phenomena in polluted industrial regions have been attributed to the breakdown of the natural chemical balance in the composition of the atmosphere[1–5]. The appearance of large amounts of toxicants in the atmosphere inevitably affects the ecosystem as a whole[6–9]. An adequate description of the chemical processes occurring in a complex reactor such as the atmosphere is possible only by resorting to mathematical models, which are capable, in conjunction with monitoring systems, of reflecting the entire wide variety of the phenomena and their interaction and permitting an assessment of the consequences of the chemical perturbations of the natural composition of the atmosphere by different sources.

Considerable progress in fundamental research into the atmosphere[10–15], in particular into the modelling of the processes of the dispersion and reactions of the natural and anthropogenic impurities in the atmosphere[16–19], has been achieved in recent years. The advances in chemical kinetics associated with the study of the mechanisms of chemical reactions has made it possible to describe the cycles of reactions of chemicals under natural atmospheric conditions and in the atmospheres of polluted industrial regions. Detailed study of the processes at the level of an elementary chemical step revealed the important role of atoms and short-lived free radicals in processes leading to the transformation of substances[10,11,20,21].

The assemblies of species playing a significant role in the reactions of chemical elements have been combined for convenience into families of O-, H-, N-, S-, C-, Cl-, Br-, and I-containing compounds[10–13]. Organic substances, the mechanisms of the reactions of which have been studied particularly vigorously in recent times in connection with the need to understand the reactions of organic impurities in air over motorways, over forests, and under the conditions of a polluted atmosphere, have been segregated in a separate group[11,12,14]. The experimental data on the chemical kinetics and photochemistry of the gas-phase reactions have been recently surveyed by an Expert Panel within the framework of the IUPAC Subcommittee for Gas-Phase Kinetics, which periodically publishes compilations of kinetic and photochemical data concerning the chemistry of the atmosphere[22,23].

A quantitative description of individual families of reactions, close to the real conditions, is achieved with the aid of mathematical models of different degrees of complexity and with different degrees of detail, depending on the aims of the studies and their practical applications[24–29]. The mathematical models based on data obtained by chemical monitoring using highly sensitive and rapid analytical methods make it possible to approach a solution to problems concerning the prediction of the chemical composition of the atmosphere on both global and local scales.

In the present review, attention is concentrated on the mathematical models used in the study of the photochemical reactions in the atmosphere. This has been done for two reasons. Firstly, the photochemical mechanism of the reactions of substances under the influence of solar radiation is the most common to all the layers of the atmosphere. It establishes the chemical composition of the atmosphere as a whole and its heat balance[2,10,11,13]. Secondly, the mathematical models for the description of photochemical reactions in the atmosphere have been fairly thoroughly developed and a great variety of them are available, which makes it possible to demonstrate the possibilities of mathematical modelling in the

solution of theoretical and applied problems in atmospheric chemistry.

II. Characteristic features of the construction of mathematical models for the description of chemical processes in the atmosphere

The laws of conservation of energy, momentum, and mass, which together with the fundamental rules of thermodynamics and chemistry describe the establishment of atmospheric motions and the transport and transformation of various substances against the background of the latter, constitute the theoretical basis of the mathematical models describing the geophysical and chemical processes in the atmosphere. In terms of mathematics, these are systems of equations for the hydrothermodynamics of the atmosphere (taking into account the transport and transformation of moisture) and systems of equations for transport processes and the reactions of impurities which describe both positive and negative feedback[17]. The complexity of the interrelations between the geophysical and chemical processes in the atmosphere as well as the incomplete knowledge of this field have led to ambiguity in the formulation of problems and in the selection of ways of solving them. The wide variety of approaches to the construction of mathematical models for the transport and transformation of impurities in the atmosphere and the principles governing their practical application have been described in fair detail in the Proceedings of the International Symposium held in 1986 in Leningrad[18].

In order to discover the characteristic features of the physical and chemical phenomena in the atmosphere, an open version of mathematical models is usually employed, in which the elements of the hydrometeorological regime in the atmospheric circulation are assumed to be known and the occurrence of chemical reactions against the background of atmospheric motions is investigated. Three cases are then distinguished depending on the relation between the characteristic chemical and dynamic time scales (t_c, d_d). If $t_c < t_d$ (for example, for short-lived atoms and free radicals), then the chemical reactions can be considered regardless of the atmospheric dynamics. On the other hand, when $t_c > t_d$, the role of dynamics is great (this happens, for example, in the study of trace species such as chlorofluoromethane, carbonyl sulphide, nitrous oxide, etc.). The case where $t_c \simeq t_d$ is most complex and the interpretation of the observations under natural conditions can therefore also be far from unambiguous (for example, for ozone and nitrogen oxides). In order to describe the behaviour (variation of the concentation) of a given impurity and to estimate its residence time in the atmosphere, it is as a rule necessary to carry out a joint analysis of hydrometeorological, physical, and chemical processes.

Analysis of the space-time scales determines the formulation of the problems of atmospheric chemistry which can be arbitrarily divided into the chemistry of the stratosphere, the chemistry of the troposphere, and the chemistry of industrial regions.

The overall structure of models of the transport and transformation of impurities in the atmosphere includes a system of equations of the following type:

$$\frac{\partial c_i}{\partial t} + \operatorname{div} c_i\mathbf{u} - \operatorname{div}_S \mu \operatorname{grad}_S c_i - \frac{\partial}{\partial z}\nu\frac{\partial c_i}{\partial z} + B_i(\mathbf{C}) = f_i, \tag{1}$$

where c_i is the concentration of the ith component at a point $\mathbf{x}$ in space at a time t, $\mathbf{u}$ the velocity vector of the air masses and impurities, μ and ν are the coefficients of the turbulent mixing of impurities in the horizontal (x, y) and vertical (z) directions, $\mathbf{C} = \{c_i(i = \overline{1, n})\}$ the impurity concentration vector, n the number of impurities, $B(\mathbf{C}) = \{B_i(\mathbf{C}), (i = \overline{1, n})\}$ the operator describing the impurity transformation processes, and $f_i(\mathbf{x}, t)$ $(i = \overline{1, n})$ are sources of impurities. The divergence and gradient operators are determined in the usual way in the selected coordinate system. The subscript S denotes operators acting in horizontal directions.

The problem is considered in the region where $D = \{D \times [0, \bar{t}]\}$, where $[0, \bar{t}]$ is the range of variation of the time t, D the region of the spatial coordinates $\mathbf{x} = \{x_\alpha, \alpha = \overline{1, k}, k \leqslant 3\}$, and k is the number of dimensions of the space.

In this case the velocity vector $\mathbf{u}$ can be represented by $\mathbf{u} = \{u_\alpha, \alpha = \overline{1, k}, k \leqslant 3\}$, where u_α is the component in the direction of the coordinate x_α. In the three-dimensional case, one usually employs the designation $\mathbf{x} = (x, y, z)$. The sources $f_i(\mathbf{x}, t)$ $(i = \overline{1, n})$ are specified as the input parameters of the model in the form of functions of spatial coordinates and time. One then takes into account sources of natural and anthropogenic origin.

To complete the description of the model, one specifies the initial and boundary conditions:

$$\text{when } z = Z_S(x, y) \quad R_{1_i}(\mathbf{C}) = f_{1_i}(x, y, t), \tag{2}$$

$$\text{when } z = H \qquad R_{2_i}(\mathbf{C}) = f_{2_i}(x, y, t), \quad i = \overline{1, n}. \tag{3}$$

Here R_{1_i} and R_{2_i} are certain operators and f_{1_i} and f_{2_i} are the sources and sinks of impurities at the $[z = Z_S(x, y)]$ and upper $(z = H)$ limits of the region D. The operators $R_{1_i}(\mathbf{C})$ describe the interaction of the impurities with one another and with the Earth's surface including the exchange processes between air, water, soil, the plant cover, etc., while the operators $R_{2_i}(\mathbf{C})$ describe the behaviour of impurities at the upper limits of the air masses. The descriptions of the operators $B_i(\mathbf{C})$, $R_{1_i}(\mathbf{C})$, and $R_{2_i}(\mathbf{C})$ are specified for each specific problem.

The conditions governing the periodicity of all the functions on the surface of a sphere and, for models designed for a limited area, the conditions governing the concentration field at the lateral boundaries are specified in terms of horizontal variables for the global model. In the vertical velocity, one takes into account the rate of gravitational precipitation of impurity particles which are heavier than air or the rise of particles which are lighter than air at the corresponding height as a result of buoyancy forces.

The first four terms in Eqn. (1) constitute the linear part of the model. The transport and turbulent exchange processes for each substance take place independently of other processes. The operator $B(\mathbf{C})$ is in the general case non-linear, describing the rate of change of the concentrations $\mathbf{C} = \{C_i, i = \overline{1, n}\}$ as a result of chemical and photochemical reactions. Since we are dealing with multicomponent impurities, the number of components n is an input parameter of the model. In practice, n is determined by the model for the transformation of impurities or by the number of substances involved in the reactions.

The hydrometeorological regime in the air masses against the background of which the impurity transport and transformation processes take place is described by the fields of the components of the wind velocity vector $\mathbf{u}$ and the turbulent exchange coefficients $\mu(\mathbf{x}, t)$ and $\nu(\mathbf{x}, t)$. In addition, the temperature, density, and

pressure fields as well as the characteristics of the humidity field, which are in general necessary for the description of the impurity transformation models and for the calculation of the reaction rates, are specified parametrically. The parameters of the hydrometeorological regime are usually assumed to be specified. Naturally, such separation of hydrothermodynamic and chemical processes in the model is extremely arbitrary and can be acceptable for relatively short time intervals and only for the sake of the simplification of the description of the overall structure and content of the impurity transport and transformation models.

The point is that in the general situation one cannot do without negative feedbacks. Many of the impurities belong to the class of optically active substances and influence the radiation processes in the atmosphere, while some influence also the moisture transformation processes, acting, for example, as condensation nuclei. All this leads to changes in the thermal and humidity-dependent processes in the atmosphere and ultimately to changes in hydrometeorological regime, i.e. in the velocity fields and in the turbulent exchange. The problem consists in the evaluation of the characteristic time scales of such negative feedbacks and of the intensity of the changes in the background processes determined by the effects of their negative feedbacks.

As a result of the modification of the formulation of the problem defined by Eqn. (1)–(3), different types of models are obtained. These modifications are determined by the following features:

the way in which the parameters of the hydrometeorological regime — the turbulent exchange models — are specified;

the procedures used to describe the boundary conditions and sources — the interactions of impurities with the underlying surface;

the choice of the space-time structure of the region, i.e. the dimensions of the problem and the hypotheses concerning the nature of the dependence of the investigated phenomena on the variables x, y, z, and t;

the procedure used to describe the impurity transformation operators;

the space-time scales of the phenomena investigated — the procedures used for a discrete description of the models and the methods of their application on a computer;

the combinations of the variants described.

An important stage in the construction of numerical models is the discrete specification of the initial problems in a differential formulation. Different procedures for such discrete specification are used nowadays — finite-difference, finite-elementary, spectroscopic, spectroscopic-difference, and their various combinations. The choice of a specific scheme is determined by the ratios of the space-time scales of the processes taken into account in the model. Together with models with rigorously determined formulations, models based on statistical modelling methods (the Monte Carlo method) are being developed.

III. Classification of models in terms of space-time scales

In relation to time, the model can be stationary or non-stationary, while in relation to spatial variables we have "point", one-dimensional, two-dimensional, and three-dimensional models.

In point (or box) models, there is no description of transport processes. Such models arise when the characteristics of the composition of the atmosphere are averaged out on the assumption of spatial homogeneity and account is taken of only stationary and non-stationary impurity transformation processes. They are convenient for the interpretation of laboratory experiments, for example in smog chambers[30–33]. Chemical processes, including all the elementary stages, are studied in detail in such models. Integration of a short time interval is used in the study of the kinetics of the reactions of reactants and products. Comparison of the results of such modelling with the results of measurements sometimes stimulates a specific search for new processes, the allowance for which would promote the reconciliation of the results of modelling and experiments[34].

One-dimensional models are usually employed when the changes in the impurity concentration fields as a result of transport and turbulent exchange are significant mainly in one direction, while in other directions once can restrict the treatment to the assumption of uniformity. This occurs, for example, in the solution of problems of the stratosphere in connection with the study of vertical motions and of problems of the boundary layer of the atmosphere over a homogeneous area of the Earth's surface[25,35–43].

1. Photochemical models of the stratosphere

The chemistry of the stratosphere is relatively simple and is described in terms of compact models. Usually 20–30 chemical species, 100–200 reactions, a temperature of 200–300 K, and a pressure of 1–100 torr are involved. The most important aspect of these problems is the photochemistry of ozone[21]. Here it is necessary to take into account four groups of species[13]: (1) "odd" oxygen O_3, $O(^1D)$, and $O(^3P)$ whose reactions are based on the classical Chapman cycle; (2) long-lived gases of tropospheric or biospheric origin, such as H_2O, O_2, N_2, CO, CH_4, H_2, CH_3Cl, CF_2Cl_2, COS, etc; (3) short-lived radicals, for example OH, HO_2, and Cl, participating in catalytic ozone decomposition cycles (we may note that allowance for these has made it possible to eliminate a number of problems concerning the ozone balance[11]); (4) the products of the reactions of short-lived radicals such as HNO_2, HNO_3, HO_2NO_2, $ClONO_2$, H_2SO_4, and H_2O_2. The most important criterion of the adequacy of such models is the agreement between the calculated and measured concentration profiles of the species most sensitive to variations in the input parameters of the models. In terms of such models, one investigates either the diurnal changes in the short-lived species or one calculates the height profile of the concentrations of the molecules averaged over long time (t) intervals. The increased interest in the chemistry of ozone in the stratosphere has led in recent years to the search for additional chemical processes which may occur in a polluted stratosphere. Thus, in order to account for the observed decrease in the amount of ozone in polar regions[26], it is necessary to resort to heterogeneous reactions involving ozone.

The attempts to understand further and to predict the changes in the content of impurities in the stratosphere under the influence of anthropogenic perturbations are nowadays based mainly on two-dimensional models which are capable of modelling the changes in concentrations as a function of two spatial variables — height and one horizontal dimension, as well as the season and the time of day. The spatial-temporal resolution and the algorithmic possibilities of such models are determined by the speed and the size of the memory of the computers employed.

Two-dimensional models are more realistic than one-dimensional models, but they too describe only individual features of the investigated phenomena. Since in recent years appreciable progress has been observed in the method for the determination of certain impurities in the atmosphere and of their dynamics, it has become

possible to compare the calculated and measured concentrations. This has stimulated a rethinking of the ideas concerning the role of certain reactions in the atmosphere.

Three-dimensional models are most consistent with the conditions in the real atmosphere. They usually combine the species transport processes, the interaction with radiation, and the photochemical reactions of the species and constitute an effective instrument for discovering the characteristic features of the establishment of the concentration profiles for impurities such as O_3, CO, CO_2, nitrogen- and sulphur-containing substances, etc. and for the determination of the level and consequences of the anthropogenic stimuli[45–48]. In three-dimensional models, much attention is devoted to their ability to describe diurnal and seasonal changes in concentration fields. Some models make it possible to calculate rapid chemical transformations of impurities on the assumption of slow changes in other parameters under the influence of external conditions. Conversely, others do not permit calculations for rapid processes but do make it possible to take into account the types of sources, sinks, and the transfer and transport of long-lived impurities. The decisive external parameters under these conditions are the concentrations of short-lived species, for example, the OH radical[13]. Models in which large averaging scales in space and time are postulated are usually employed for climatic predictions.

Much attention has been devoted recently to the development of three-dimensional models for the study of the chemistry of the polluted atmosphere of industrial regions[44–61]. The multiplicity of approaches to the construction and application of such models have been tried. Thus models of the dispersal of impurities arising from powerful sources take into account the transport processes on a regional scale but neglect the details of the chemical transformations. Local models of the "quality of air" include the chemistry of atmospheric contaminants usually with parameterised decriptions of the transport processes. Such models are as a rule designed for ecological predictions on a regional scale (including different countries).

Table 1. Classification of the models in terms of characteristic space-time scales of the processes and typical problems solved with the aid of the models.

Horizontal scale, km	Vertical scale, km	Specific features of ecological problems
1–10	1–5	Influence of open-cast mining, chemical and aerosol methods in agriculture, and large industrial units on the environment
10–100	5–10	The microclimate and pollution of urban atmospheres
10–100	10–20	Effect of powerful anthropogenic heat sources on the environment with evolution of polluting impurities
100–1000	10	Environmental protection problems for large territorial-industrial complexes and influence of large hydrotechnical units on the hydrothermodynamics of the atmosphere
1000–10000	10	Studies on the cyclogenesis and the long-range transport of impurities
Global	10–30	Energy and mass exchange in climatic system and the global transport of impurities in the atmosphere

Questions concerning allowance for feedback effects, which arise in the joint consideration of chemical processes together with processes involving the hydrothermodynamics of the atmosphere may be regarded as little developed aspects of three-dimensional models. The construction of complex models greatly complicates the formulation of the problem and requires the solution of the problem of a self-consistent description of processes on different space-time scales. Thus the specific problem and the range of phenomena considered dictate the choice of the structure of the model, its discrete analogues, and the methods of parametrising chemical and physical factors. Table 1 presents a classification of models in terms of space-time scales, which provides an idea about certain possible combinations of hydrothermodynamic models with models of the chemical transformations of mixtures.

The technology of the modelling of chemical processes in the atmosphere consists of several stages, which are common to the majority of models. The structure of numerical algorithms for the application of the model on a computer depends in many respects on the choice of a particular transformation mechanism (photochemical mechanism, reactions in drops, heterogeneous reactions, combustion processes), in order to take into account in the model of the atmosphere, and on the degree of its development.

The modelling of a photochemical process consists of the following stages.

1. The formation of a data base of reaction rate constants and establishment of a system of kinetic equations.
2. Determination of the dependence of the rate constants on temperature, pressure, intensity of solar radiation, moisture, etc.
3. Establishment of a system of differential equations describing the kinetics of the processes.
4. Analysis of the characteristic time scales of the chemical reactions and estimation of the lifetimes of the species taken into account in the system of equations.
5. The study of the properties of the solution of the system of differential equations for specified reaction rate constants and initial concentrations of impurities.
6. Analysis of the sensitivity and the stability of the defining equations with respect to variations in the input parameters.
7. The selection of a scheme for the integration of the system of equations for the transformation of impurities. The study, on the basis of an analysis of the time scale and of the sensitivity of the model to variations in the input parameters, of the possibility of the "contraction" of the system of equations in terms of a specified criterion with retention of the material balance and of the properties of the solution.
8. Interpretation of the results of numerical modelling and their comparison with data derived from experimental studies and measurements under natural conditions. If necessary, the parameters of the models can be identified on the basis of factual information.

It is noteworthy that problems concerning the mathematical modelling of chemical processes occurring in the atmosphere are of independent interest from the standpoint of computational mathematics[17]. The systems of differential equations for their description are as a rule non-linear. The number of reactions in real problems may reach several hundreds and they occur at each point in a three-dimensional region against the background of relatively slow hydrothermodynamic circulation of the atmosphere. The reaction rate constants differ by several orders of magnitude. The systems of defining differential equations can be classified in terms of their properties as so called "stiff" systems. All the foregoing factors indicate the complexity of the solution of such problems on modern computers.

One of the convenient methods for the algorithmic application of the models is the cleavage method. The method is interesting because it makes it possible to model processes over a short time

interval in such a way that in one stage the calculation of transport proceeds in parallel and independently for each species throughout the region, while in another the set of systems of equations describing the transformation of the impurities at each point in space is solved for all the species simultaneously and independently of their solution at other points. Such organisation of the model makes it possible to reconcile the characteristic scales of different processes and to facilitate significantly the solution of problems of the parametrisation of impurity transformation processes when their characteristic time scales are short compared with the steps used in the specification of the model in a discrete form as a function of time. The computational algorithms then obtained are simple to apply and economical as regards the number of arithmetical operations.

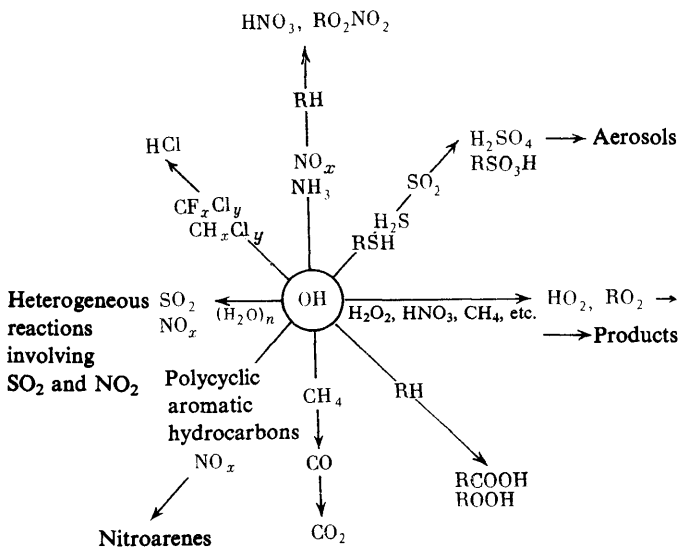
2. Photochemical models of the troposphere

The chemical models of the troposphere are much more complex than the stratospheric models for a number of reasons. Firstly, much more complex impurity transport and diffusion processes take place in the troposphere, in which turbulence, characterised by a marked spatial-temporal variability, plays an important role. Secondly, owing to filtration by the ozone layer, only light at wavelengths longer than 290 nm penetrates into the troposphere. The primary photochemical processes therefore take place in the troposphere with different rate constants. Among them, the reactions involving the photolysis of ozone and of nitrogen oxides with formation of atomic oxygen are the most important. The reaction of $O(^1D)$ with the admixtures of water vapour in the atmosphere, i.e.

$$O(^1D) + H_2O \rightarrow 2OH$$

to form the hydroxyl radical OH, plays a key role in the chemistry of the troposphere (Scheme 1)[10-12]:

Scheme 1



The quantitative and qualitative composition of the impurities in the troposphere is incomparably more varied than in the stratosphere. There are considerable differences between the compositions of the atmosphere in the layer near the Earth's surface over different regions. Fig. 1 compares the concentrations of impurities typical for the air of unpolluted and industrial regions. The horizontal lines indicate the levels of the maximum permissible concentrations (MPC) recommended as health norms for quality of the atmosphere. Fig. 1 shows that the concentrations of the impurities vary by several orders of magnitude in both unpolluted and polluted atmospheres. The chemical compositions of the impurities in air over the oceans, forests, and desert are usually significantly different.

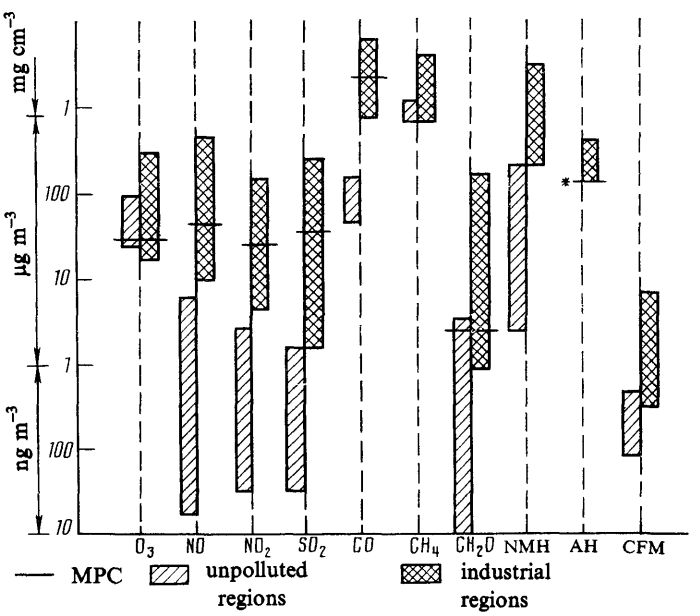


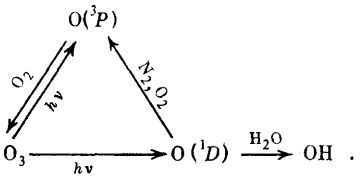
Figure 1. Concentrations of typical impurities in the air of unpolluted and industrial regions: NMH—non-methane hydrocarbons; AH—aromatic hydrocarbons; CFM—chlorofluoromethanes. *The maximum permissible concentration (MPC) of xylene, the most widely distributed aromatic hydrocarbon in cities, is indicated[8,14,15,62,63].

The concept of the "background" atmosphere, whose composition is recommended as a reference standard for the estimation of air quality, has therefore been adopted. In a polluted atmosphere, one uses for this purpose the values of MPC which can be adopted by convention as a norm of the "purity" of the polluted air. The modelling of chemical processes in the background and polluted atmospheres in different regions therefore constitutes problems with different degrees of complexity and the input parameters for their solution must be based on data for the composition of air in both the background atmosphere and the polluted atmosphere of a particular region.

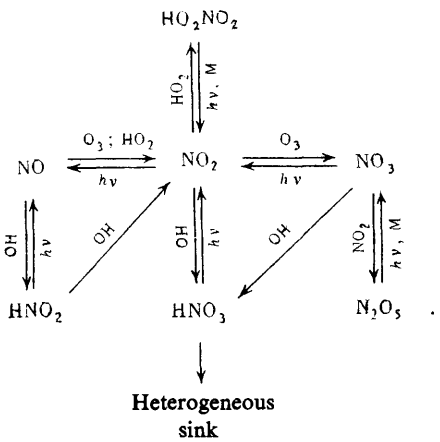
(a) The background troposphere. The chemistry of the background troposphere is in many respects similar to the chemistry of the stratosphere. Thus the same reactions (Scheme 2–4) take place in the families of the O-, N-, S- and C-containing compounds as in the stratosphere, but the number of possible reaction pathways is greater and additional species appear as a consequence of the greater variety

of the impurities and of their concentrations in the troposphere. We may note that the halogens are actively involved in the chemical reactions occurring in air over the seas[10,13,49,63].

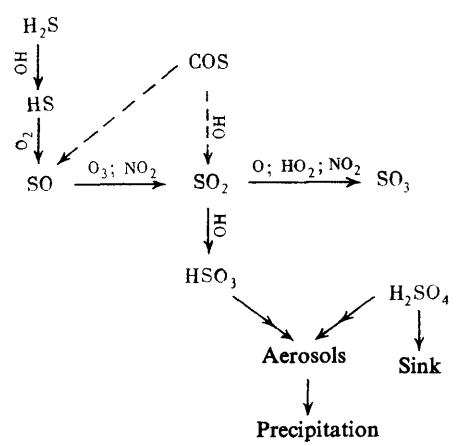
Scheme 2



Scheme 3



Scheme 4



Organic compounds occupy a special place in the photochemistry of the troposphere. Whereas only a few of relatively stable substances at low concentrations (for example, chlorofluoromethanes, carbonyl sulphide) penetrate into the stratosphere from the Earth, in the troposphere the situation is significantly different. An insignificant increase in complexity compared with the stratosphere is observed only in the atmosphere over the seas. Owing to the presence of terpenes in the air over forests, the scheme of the transformations of the impurities is supplemented by the reactions of terpenes with ozone and nitrogen oxides[63,64].

Hydrocarbons in general differ sharply in their reactivities and reaction mechanisms from other compounds. Their potential capacities to generate secondary contaminants are also not the same.

In such situations, it is necessary to take into account the multicomponent nature and the pronounced spatial-temporal non-uniformity of the distribution of these compounds. In the study of the photochemistry of the troposphere in the 1970s, the consideration of individual organic compounds was therefore replaced by the study of multistage photochemical mechanisms[32]. Proof of the validity of this treatment of atmosphere chemistry was obtained in numerous kinetic laboratory experiments and in smog chambers both in the investigation of simple mixtures and for real waste products[30,53,65–67].

Analysis of the results obtained in carrying out the programme of the Global Tropospheric Experiment[68–70] in order to test the existing photochemical models confirmed in many respects the validity of the ideas about the photochemistry of the atmosphere and has raised a number of problems requiring a more detailed study. Investigations of the atmosphere over polluted regions in order to develop a strategy for the monitoring of air in the atmosphere using mathematical modelling for such purposes belong to the range of studies of greatest current interest.

(b) Models of the atmosphere over polluted regions. The monitoring of the composition of the atmosphere over polluted regions revealed a series of factors which require interpretation, especially under smog conditions. Apart from carbon monoxide, nitrogen oxides, sulphur dioxide, and hydrocarbons, which are present at increased concentrations in automobile transport exhausts, in the flames generated in thermal electric power stations, and elsewhere, substances which are not characteristic of the primary industrial waste were also recorded, for example, peroxynitrates, organic sulphur- and nitrogen-containing compounds, organic acids, and peroxides. Furthermore, anomalies were noted in the diurnal variation of the concentrations of ozone[11,12,15,71]. This shows that secondary photochemical oxidants are formed in all kinds of photochemical smog[11,26,51,53,57].

Models of the chemistry of the atmosphere in areas with an increased anthropogenic input, characteristic of industrially developed regions, make it possible to describe the dynamics of the appearance and development of smog situations. As an example, we shall describe briefly one such model of the transport and transformation of impurities against the background of the hydrometeorological regime of an industrial region[17,72,73]. Its structure is typical for models of this class known in the literature[18,19]. Two versions of calculations are usually employed—in the linear and non-linear approximations, and the model is as rule tested in relation to the most typical waste ejected into the atmosphere in industrial regions—SO_2, NO, NO_2, CO, CH_4, and CH_2O. The chemical reactions of these compounds are initiated by sunlight which results in the activation of photoactive molecules, for example, SO_2, NO_2, and CH_2O. Atoms and free radicals as well as certain products together with the initial waste participate in the intermediate stages of the chemical reactions.

The linear approximation is based on the application of the method of quasi-stationary concentrations of active species (atoms, free radicals, and electronically excited molecules). The reaction rate constants used in the calculations are available in familiar handbooks on atmospheric chemistry[22,23,74]. Apart from atoms and free radicals, the photochemical reactions result in the appearance and accumulation of products which were not present in the initial

waste, for example, nitric, nitrous, and sulphuric acids as well as hydrogen peroxide.

The non-linear model is used in calculations for the set of reactions of nitrogen, sulphur-, and carbon-containing compounds most characteristic of the atmosphere in industrial regions.

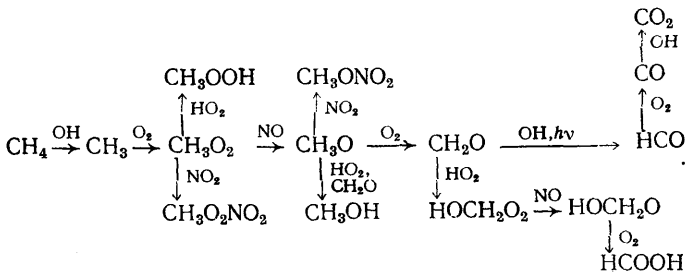
In mathematical models, there is a possibility of different modifications in the descriptions of the mechanisms of the transformation of organic compounds. A classification of hydrocarbons into three groups was adopted in 1977: alkanes, alkenes, and aldehydes[32]. Aromatic compounds have not been considered separately hitherto. Among all these compounds, the photochemistry of methane has been studied in greatest detail in view of its possible climatic consequences[2,75,76].

For these purposes, a simplified scheme of the reactions of methane is usually considered:

$$CH_4 \rightarrow CH_2O \rightarrow CO \rightarrow CO_2 .$$

It is employed, for example, in global models in estimating the greenhouse effect. High concentrations of CH_4, CH_2O, and CO and more complex combinations of impurities in the polluted atmosphere require a more complete methane oxidation scheme (Scheme 5). This is necessary in the assessment of the overall toxicity of the air in polluted regions. Analysis of the results obtained within the framework of both simplified and complete methane oxidation schemes[73] revealed the necessity to increase the number of methane reactions considered under the conditions of polluted air. The complete computational scheme takes into account about 200 elementary stages, while in the simplified scheme the number of such stages is only 40.

Scheme 5



As a consequence of the non-linearity of the problem being solved, it is of interest to elucidate the influence of the level of waste products on the final chemical composition of the contaminated air. Certain examples of such calculations are presented below. In the first of these (Fig. 2), the amount of CH_4 waste varies over three orders of magnitude. It is found that the increased amount of methane emitted is accompanied by a non-linear growth of the concentrations of peroxides, formic acid, and carbon dioxide. The dependence of the yield of products on the amount of formaldehyde waste is more complex (Fig. 3). The concentrations of many intermediate and final products [$O(^3P)$, O_3, OH, HO_2, NO_3, CH_3O_2, H_2O_2, CH_3OH, CH_3OOH, HCOOH, HNO_2, HNO_3, HO_2NO_2 (Fig. 4)] are influenced by the level of waste nitrogen dioxides. The dependence on NO_x is non-linear. This is manifested in two ways: the content of the acids HNO_2 and HNO_3 increases and that of other products—peroxides, organic acids, and peroxynitrate—falls. The concentration of ozone changes little under these conditions, because only the NO_2/NO ratio is important in determining it.

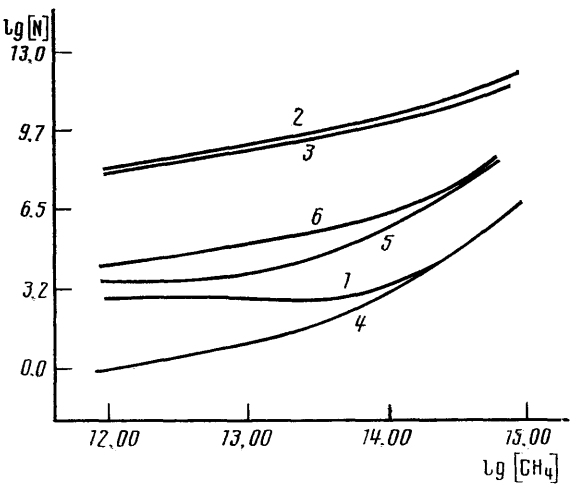


Figure 2. Logarithmic dependence of the formation of H_2O_2 (curve *1*), CH_2O (curve *2*), CO (curve *3*), CH_3OOH (curve *4*), HCOOH (curve *5*), and CO_2 (curve *6*) on the methane concentration (cm^{-3}) for t = 12 h (the accompanying concentrations are 10^{11} cm^{-3} for NO_x and 2.6 × 10^{11} cm^{-3} for O_3) [73].

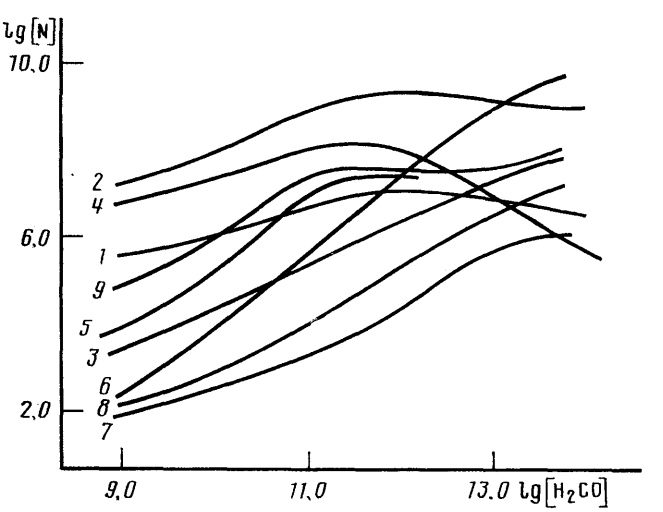


Figure 3. Sensitivity of the OH (curve *1*), HO_2 (curve *2*), CO × 10^{-7} (curve *3*), CH_3O_2 (curve *4*), CH_3OOH × 10^{-3} (curve *5*), HCOOH × 10^{-4} (curve *6*), CH_3ONO_2 × 10^{-4} (curve *7*), HO_2NO_2 × 10^{-5} (curve *8*), and CH_3OH (curve *9*) concentrations to variations in the amount of formaldehyde on the logarithmic scale for t = 12 h (accompanying concentrations 10^9 cm^{-3} for NO_x and 3 × 10 cm^{-3} for CH_4) [73].

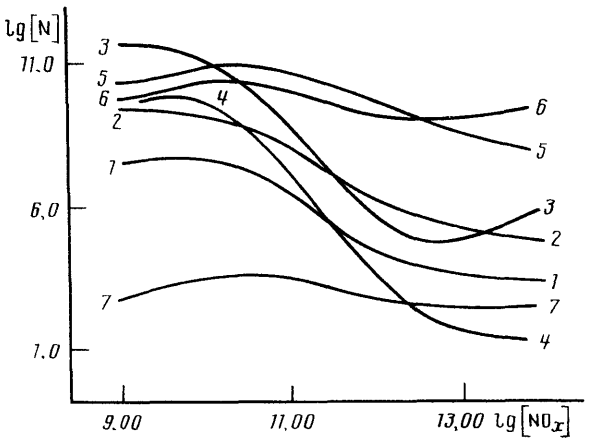


Figure 4. Sensitivity of the CH_3O_2 (curve *1*), HO_2 (curve *2*), H_2O_2 (curve *3*), CH_3OOH (curve *4*), HCOOH (curve *5*), HO_2NO_2 (curve *6*), and CH_3O (curve *7*) concentrations to variations in the amount of NO_x on a logarithmic scale for t = 12 h (accompanying waste products 2 × 10^{13} cm^{-3} for CO, 3 × 10^{13} for CH_4, and 2.4 × 10^{11} cm^{-3} for CH_2O) [73].

Fig. 5 shows that under polluted conditions, the diurnal variation of the concentration of OH radicals did not follow exactly the diurnal movement of the sun in the chemistry of both the stratosphere and the background troposphere—its maximum may be observed also at other times in the morning and in the evening.

Thus consideration of the photochemical oxidation of methane alone in a polluted atmosphere shows how great is the increase in the complexity of both the problem itself and of the conclusions reached on its basis and of their interpretation. Fig. 6 presents an example of such a calculation under urban conditions.

Experience has shown that one cannot transfer mechanically the results of calculations, obtained using a model adapted to a particular region, to other regions. The marked non-linearity of the process (i.e. the dependence on the concomitant impurities, for example nitrogen oxides) does not allow the fitting of simple relations to its rate.

The photochemical model was developed further in the 1980s when a data base for non-methane hydrocarbons was created, which made it possible to introduce the latter into the mathematical models for different levels[28,76–81]. As a consequence of this, the degree of understanding of the principal features of the dynamics of photochemical smog increased. A special place has been assigned recently to the chemistry of the nighttime atmosphere as an after-effect of the daytime photochemistry. In these processes, a leading role is attributed to the NO_3 radical, whose maximum concentrations are observed in the atmosphere after sunset[22].

Since the majority of the models involve very laborious computations, one usually endeavours to simplify as far as possible the schemes for the chemical reactions of organic impurities. It is noteworthy that, before simplifying the reaction scheme, it is desirable to carry out calculations within the framework of the most complete scheme and to make sure with the aid of tests that the simplified scheme reproduces the principal results in conformity with the aims of the investigations.

Calvert and Madronich[79] recently examined the detailed chemical mechanism of the oxidation of hydrocarbons in the atmosphere. It included 26 alkanes (C_1-C_8), alkenes (ethylene and propene), aromatic hydrocarbons (benzene, toluene, and xylenes), and terpenes (isoprene and α-pinene). It was shown that, in the absence of NO_x at appreciable concentrations in the atmosphere, the oxidation products are significantly different. A rigorous specificity of the products, their concentrations, and their lifetimes is expected for each class of hydrocarbon depending on the conditions, which may serve as a useful indicator of the behaviour of air masses as a function of time.

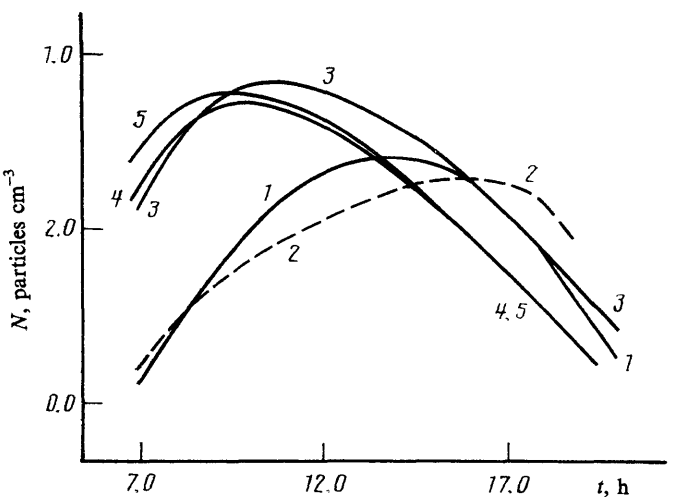


Figure 5. Diurnal variation of the concentrations of the hydroxyl radical OH as a function of the NO/NO_2 ratio (accompanying concentrations 3 × 10^{13} cm^{-3} for CH_4, 2 × 10^{13} cm^{-3} for CO, and 2.4 × 10^{11} cm^{-3} for CH_2O): *1*, [OH] = 0.5 × 10^{-6} cm^{-3} (10^{14} cm^{-3} for NO, 10^{12} cm^{-3} for NO_2); *2*, [OH] = 2 × 10^{-6} cm^{-3} (10^{13} cm^{-3} for NO, 10^{12} cm^{-3} for NO_2); *3*, [OH] = 0.4 × 10^{-5} cm^{-3} (10^{12} cm^{-3} for NO, 10^{12} cm^{-3} for NO_2); *4*, [OH] = 3 × 10^{-6} cm^{-3} (10^{11} cm^{-3} for NO, 10^{12} cm^{-3} for NO_2); *5*, [OH] = 0.8 × 10^{-6} cm^{-3} (10^{11} cm^{-3} for NO, 10^{11} cm^{-3} for NO_2). {Note by Ed. of Translation: all exponents for [OH] should be positive not negative}.

Another aspect of the chemistry of organic substances in the atmosphere was developed by Atkinson and co-workers[74,77,78]. Comparison of the reactivities (rate constants for the reaction of the OH radical) with the physicochemical properties of organic molecules (ionisation potentials, electrophilic substitution constants, etc.) yielded empirical relations for the calculation of the rate constants for reactions of compounds of different classes with free radicals and ozone. Correlations were discovered between the rate constants for reactions occurring between the OH radical and $O(^3P)$ and also between the NO_3 radical and ozone. This approach makes it possible to estimate the rates of reactions and the lifetimes of many organic compounds and their homologues in the atmosphere and to formulate the principal schemes for the reactions of organic impurities in a polluted atmosphere.

Theoretical studies in the field of tropospheric chemistry of organic compounds have served as a basis for the estimation of the potential toxicity of the entire set of impurities. They are useful in the consideration of pathways leading to the decomposition of substances, for the estimation of their lifetimes in the troposphere, and for the possibility of the appearance and further transformation of secondary products.

IV. Analysis of the sensitivity of the models

The study of the sensitivity of the models to variations in the input parameters and in the rate constants for individual reactions is an essential stage of numerical modelling. It includes the calculation of the partial derivatives of a specified set of characteristics and the estimation of the changes in the functions of state of the model process in terms of the investigated parameters. Here several approaches are used, which make it possible to elucidate the relative significance and the degree of uncertainty in individual stages of the complete scheme, the possibility of its simplification, and also the trends in the development of the principal relations[67,76,83–91]. Such approaches include the direct modelling method, methods based on the solution of variational problems, variational methods using coupled problems, and modelling of the response of the system to specified perturbations.

The simplest and frequently employed procedure is the direct modelling method. It is based on repeated solutions of the defining system of equations with variation of the input parameters. However, repeated solutions become impractical in complex systems with many parameters.

The principal uncertainty in the photochemical mechanism involves the estimation of the rate of photolysis of compounds under real conditions. A clear example is provided by the photolysis of acetone. It was found that in the atmosphere the quantum yield of this reaction is only 0.08–0.15 [69] instead of 1, obtained under laboratory conditions[92]. Demerjian et al.[92] tabulated certain data in the photolysis of a number of molecules as a function of the latitude and the zenithal angle under real atmospheric conditions, but the absorption cross-sections of the molecules and the quantum yields of the photochemical reactions of many compounds have not yet been adequately investigated. The uncertainty is enhanced by the hydrometeorological conditions, for example, the cloud cover.

Whereas the rate constants for reactions involving inorganic compounds have been studied in fair detail, as regards reactions with organic impurities there are considerable uncertainties both in the rate constants and in the products themselves. In 1979, Seinfeld and co-workers[83] analysed the uncertainties in the photochemical mechanism and outlined the priorities in their investigations. Over ten years, there has been considerable progress in these fields: the reactions of ozone with alkenes and the products formed under these conditions were investigated in detail and the parameters of the formation and decomposition of peroxynitrates were refined. In the field of the reactions of aromatic compounds in the atmosphere, qualitatively new and important information has appeared[11,12,23,71,77,93]. The progress which has occurred in the measurement of photochemically active impurities in the atmosphere has made it possible to determine with greater accuracy the initial parameters of the models[68–71].

Analysis of the sensitivity and uncertainty of individual stages of the complete reaction scheme is a useful aid to the formulation of experiments and identification of the parameters exerting the greatest influence on the quality of the prediction. The "counter species" technique has been used[28] for the analysis of complex mechanisms with a large number of stages which makes it possible to test the internal self-consistence of the complex reaction mechanism under different conditions.

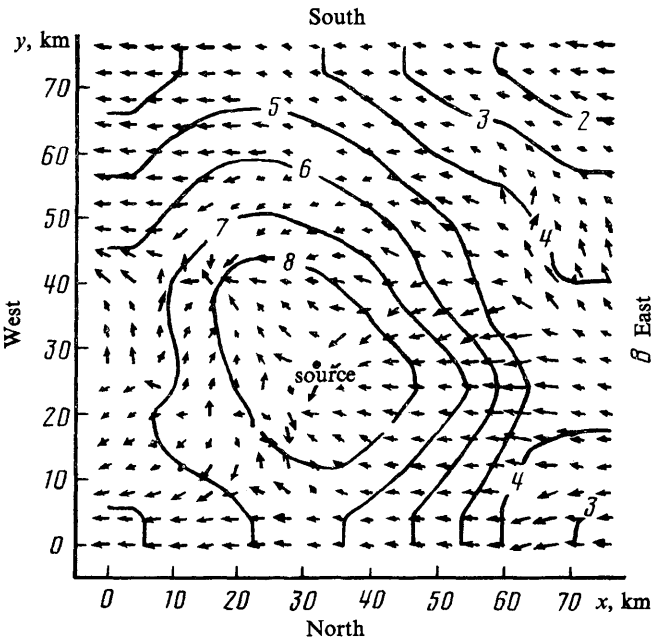


Figure 6. Contours for the variation of the concentrations (continuous lines) of hydrogen peroxide H_2O_2 (on a logarithmic scale) and of the vector field $\mathbf{V} = |V^2 + U^2|$ (arrows) for $t = 12$ h under urban conditions[73].

Studies on the sensitivity of different schemes used in models have thrown light on many questions, for example, on the contribution of aldehydes and aromatic hydrocarbons to the conversion of NO into NO_2, and have made it possible to compare several versions of the schemes describing the system and to formulate the principles of the arrangement of hydrocarbons in groups without prejudicing the quality of the prediction.

V. Models of chemical reactions of impurities in drops and clouds

One of the serious global problems is the formation of acid residues as a consequence of the pollution of the atmosphere by gaseous impurities, which lead to the formation of acid products—the inorganic acids H_2SO_4, HNO_2, and HNO_3, and organic acids, for example HCOOH. Recently the problems of the modelling of such processes have been attacked vigorously[76,94–97]. The gas-phase photochemical reactions examined above precede the acidification reactions and the alteration of the chemical composition of drops. In these models, it is essential to consider in addition the

processes involved in gas–liquid phase equilibria[11,98] and to take into account the possibility of the occurrence of heterogeneous and liquid-phase reactions. For example, in the interpretation of the results of observations in nature for the content of sulphate in precipitates, it proved insufficient to examine only the gas-phase transformations of sulphur dioxide into sulphates with subsequent dissolution and the concept of the chain mechanism of the oxidation of sulphur dioxide in the liquid phase was therefore invoked[99].

The oxidation of NO_2 to HNO_3 in clouds is now considered not only from the standpoint of photochemistry but to a large extent the idea of the reactions of nitrogen oxide in the dark, the so called "night chemistry"[82,97], is also invoked.

Overall, mathematical models throw light on the characteristic features of the formation of acid deposits and their transport processes on both global and regional scales and reveal the possible ecological consequences of these precipitations, for example, the causes of the large scale destruction of forests[3,5].

It is noteworthy that a specific feature of the construction of these models involves the need to build into the model the occurrence of microphysical moisture transformation processes in the atmosphere, self consistent in terms of space-time scales, which itself constitutes a fairly complex physico-mathematical problem.

VI. Characteristic features of the mathematical models of the photochemical formation of aerosols

Phenomena in the climatic systems such as the existence of an aerosol layer is the upper troposphere (for example, the Junge layer) and the decrease in the transparency of air in regions with increased gas-phase pollution are associated under certain conditions with aerosol formation processes under the influence of light[4,11].

The precursors of the relatively involatile products (stimulators of the formation of aerosols) are gas-phase photochemical reactions whose modelling was considered above. The modelling of aerosol formation is therefore a natural development of the models of the transformation of impurities designed to follow the sections of geochemical substance transformation cycles occurring in the atmosphere from the instant of their formation to the instant of their disappearance, because the concentrations of impurities in air are a result of a dynamic equilibrium between their sources and sinks.

For the modelling of the kinetics of the formation of atmospheric aerosols and the establishment of their particle dimensions and chemical composition, it is necessary to take into account the chemical processes leading to the appearance of aerosol products, the transport of gases to the surfaces of the particles, the appearance of new particles as a result of nucleation and coagulation, and equilibrium between the particles and the local gas composition of the medium[11]. The key problems in the modelling of the evolution of the urban aerosol have been solved in a series of studies[52,58,100–105]. The combination of such a model with a three-dimensional model of atmospheric dynamics has made it possible to compare the results of calculations with measurements in nature. The model predicts the daytime and nighttime compositions of the inorganic aerosols for different humidities and permits the estimation of the influence of volatile organic components. For example, it has been concluded that the formaldehyde impurity in clouds inhibits the formation of sulphates and stimulates the formation of formic acid[106]. A sectional model of aerosol dynamics has been developed[107] and the results of modelling have been compared with the results of experiments carried out in smog chambers.

VII. The use of mathematical models for monitoring the quality of air

This section presents certain examples of the application of mathematical models using the photochemical mechanism in the development of a strategy for monitoring the quality of air.

The involvement of sulphur dioxide in the photochemical mechanism has been analysed[53,108]. Determinations, under natural conditions, of the structure and evolution of a plume which contains SO_2, NO_x, and hydrocarbons are inherent in the model taking into account both the photochemistry and the transport processes of these compounds. The rate of conversion of sulphur dioxide into sulphates usually observed in a polluted atmosphere increases from 1–4% per hour (in plumes with a high content of hydrocarbons) to 12–13% per hour. Comparative analysis of the results of measurements and calculations yielded a satisfactory explanation of the sharply rising rate of oxidation of SO_2. It is attributed to the notable influence of hydrocarbons on the transfer of the chain reaction from hydroxyl radicals to peroxy-radicals. It is to be expected that this mechanism can lead to an increase in the rate of reaction of SO_2 to 40% per hour[99].

An especially large amount of attention has been devoted to the elucidation of the problem of the formation of ozone in the atmospheres of polluted regions[12,55,60–62,89,108]. This is due to the fact that ozone belongs to the class of the most significant indicators of air quality and is a representative measure of the secondary pollution of the atmosphere as a result of photochemical reactions[44,45,108–113].

Models corresponding to different levels are used to investigate the chemistry of ozone. Thus the dependence of the concentration of ozone on the ratio $[HC]/[NO_x]$ was investigated in a study[56] where twelve hydrocarbons (HC) were considered. It was found that, for low values of this ratio, the nature of the hydrocarbons themselves is important, while for high values the formation of ozone is limited by the concentration of nitrogen oxides. In another model[55], account was taken of 37 hydrocarbons, 169 species, and 320 reactions. Here attention was concentrated on the characteristic features of the hydrometeorological regime in the atmosphere and on different concentrations of the gases in the sources of pollution. The contribution of individual sources and of different classes of compounds to the formation of ozone was estimated. It was concluded that the exhausts from automobile transport is the most important source.

A regional model, whose development was initiated by the observation of anomalous concentrations of ozone in the atmospheres of polluted regions, constitutes the basis of a strategy for the monitoring of exhaust waste products in the USA. It describes the dynamics of atmospheric and chemical processes on different scales—from global to local. The content of ozone and its diurnal variation are being predicted and the sources (ozone precursors) not taken into account hitherto are being discovered. The very detailed specification of the model helps in its employment for practical purposes on a regional scale[44,45].

A model proposed by Thompson et al.[89] is devoted to the problem of the chemistry of ozone in the troposphere. Here emphasis is laid on the interrelation of the consequences of pollution by methane, carbon monoxide, and nitrogen oxides. It was shown how specific features of the injection of one impurity lead to changes in the concentration of O_3, which depends on the level of the remaining impurities. A hybrid model has been developed[108] for the estimation of the behaviour of waste products from different point sources.

It combines the treatment of data obtained in measurements under natural conditions with subsequent calculation. The conclusions for the development of a monitoring strategy and for the improvement of the quality of the prediction are that in smog situations the normalisation of the ozone content requires in the first place a decrease in the amount of non-methane hydrocarbon waste, while the level of pollution by nitrogen oxides is less important. This conclusion concerning the priority of measures to be taken to reduce the hydrocarbon waste products was reached also in other investigations. Studies in recent years have demonstrated the importance of monitoring hydrocarbons in order to develop the optimum strategy for the improvement of air quality.

A scientific strategy for the monitoring and control of air quality has been developed on this basis. The use of mathematical models combined with a monitoring system makes it possible to predict the chemical situation and to elucidate the key features in its establishment and also to formulate the necessary program of observations. In the development of measures to protect nature, mathematical models constitute a convenient instrument for reconciling economic, chemical, geophysical, and other aspects of this problem.

VIII. Conclusion

Thus mathematical modelling helps to expand the possibilities of studying the reactions of chemical compounds starting from the instant of their entry into the atmosphere to their removal from the atmosphere. Further progress in atmospheric chemistry can be achieved provided that programs for experimental measurements of the chemical composition of the atmosphere and of the rates of chemical reactions are improved and also provided that combined chemical and hydrothermodynamic models are developed in order to investigate the turnover of substances and the interaction of chemical and geophysical processes in the atmosphere. The joint consideration of atmospheric processes together with the dynamics of chemical reactions makes it possible to specify the phenomena which are responsible for the reactions of chemical substances under the influence of natural and anthropogenic factors.

Numerical modelling is used widely as an instrument for the study and development of a strategy for the monitoring of pollution and for the improvement of the quality of air in order to prevent negative ecological consequences. Since this problem has many aspects and is interdisciplinary in character, a promising approach to its solution involves the creation of expert systems for the control of the quality of the natural environment based on logical mathematical models of physicochemical and climatic processes coupled with an ecological monitoring system.

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