photodissociation of these two compounds by troposphere ultraviolet radiation was found to be extremely low.

The prediction in relation to the third compound, $C_2F_4Br_2$, is more realistic. The extent of light absorption in the 300 nm region was found to be low (10^{-22} cm^2) but adequate, so that $C_2F_4Br_2$ underwent photodissociation primarily in the troposphere. Nevertheless on account of the significantly greater efficiency of bromine particles in comparison with chorine particles the hazard of $C_2F_4Br_2$ was found to be greater than that of for example Freons 11 and 12.

Thus the problem of the assessment of the hazard of alternative compounds can be considered to be correctly set up but further studies are necessary in order to resolve this problem.

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Translated from *Uspekhi Khimii* **60** 514–520 (1991)

Mathematical modelling of the distribution of atmospheric contaminants taking account of chemical transformations

N M Bazhin, V V Penenko, A E Aloyan, G N Skubnevskaya
Institute of Chemical Kinetics and Combustion, Siberian Section of the Academy of Sciences of the USSR, Novosibirsk

The troposphere is the layer of the atmosphere adjacent to the surface of the Earth. Although the altitude of this layer is small, no more than 11 km, it plays a dominant role in the chemical processes which take place in the atmosphere. Various chemical impurities enter the troposphere, originating both from the Earth's surface as a result of natural geological, biological, chemical and physical processes, and from the upper layers of the atmosphere. In recent years, a considerable proportion of substances entering the troposphere have stemmed from anthropogenic influences, their strength being in some instances comparable to that of natural sources. A very important outcome of the anthropogenic influences is the emission into the atmosphere of substances which either do not occur in the natural state, or have until now been present in very small concentrations as, for example, freons. This may have completely unexpected and hardly foreseeable consequences.

On entering the atmosphere, the impurities become immediately involved in processes of two types:
(a) physical dilution and transport caused by different processes of diffusion and motion of air masses;
(b) chemical transformations.

The aim of the present work is to describe secondary mechanisms of atmospheric pollution, associated with the chemical transformation of impurities in the troposphere, and modelling of these mechanisms combined with hydrometeorological processes.

1. Chemical transformation of substances in the troposphere

Let us consider the possible ways of chemical transformation of substances in the troposphere. The following can be regarded as the main impurities in the troposphere: O_3, CO_2, CO, NO, NO_2, NH_3, CH_4, H_2, SO_2, CH_2O, H_2S, etc.[1] Under typical conditions (at a temperature of 25 °C) all these substances are stable enough. With few exceptions, they do not react with each other or with the main components of the atmosphere. A typical exception is apparently nitric oxide, capable of entering the reaction

$$2NO + O_2 \rightarrow 2NO_2,$$

However, the rate of this reaction, too, is insignificant as long as the NO concentration is low. Nevertheless, chemical transformations in the atmosphere do occur.

The main reason for these chemical reactions is the effect of solar radiation on constituents of the atmosphere.[2] The spectrum of solar radiation measured at the Earth's surface and in the stratosphere, is shown in Fig. 1. It is clear from it that only photons with wavelengths in excess of 300 nm reach the surface of the Earth. Thus in the troposphere photochemical dissociation of oxygen, and even to a greater extent that of nitrogen, into atoms is impossible, although some impurities may undergo photolysis. Table 1 presents some information on these components.[3]

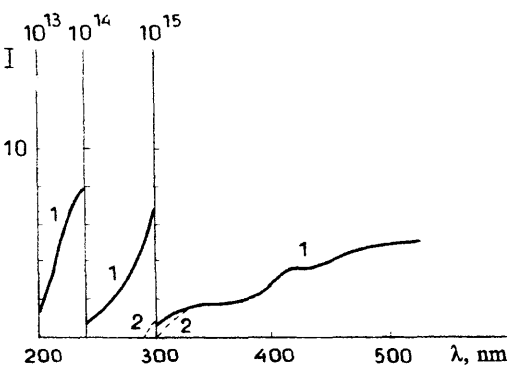


Figure 1. Spectrum of solar radiation.[3] *I* is the number of photons per second reaching an area normal to their propagation: *1*, in the stratosphere; *2*, at the Earth's surface.

It can be seen from the table that the number of substances undergoing photochemical dissociation in the atmosphere is small. Yet some of these substances, for example, HNO_2, H_2CO, NO_2, and O_3, may exhibit very high dissociation rates, their lifetimes in the troposphere being as short as a few hours. However, not all these processes play an important part in the elimination and transformation of tropospheric substances, since the path a particular substance has entered the atmosphere is also important. For example, the photolysis of nitrous acid HONO, which proceeds at a high rate, leads to the formation of OH and NO radicals, but then nitrous acid itself is formed in the atmosphere (if one excludes its anthropogenic origin) as a result of the reaction between OH and NO particles:

$$OH + NO \rightarrow HONO.$$

Therefore, the formation of HONO represents more of a sink of OH radicals than a source of them, so that a physically maintained equilibrium should exist in the troposphere

$$OH + NO \underset{h\nu}{\rightleftarrows} HONO.$$

Table 1. Chemical transformations of substances in the troposphere.

Substance	λ, nm	Photochemical reactions	Quantum yield
O_3	440÷850	$O_3 \rightarrow O(^3P) + O_2(^3\Sigma)$	~1
	300÷360	$O_3 \rightarrow O(^3P) + O_2(^1\Sigma \text{ or } ^1\Delta)$	~1
	200÷320	$O_3 \rightarrow O(^1D) + O_2(^1\Delta)$	~1
H_2CO	300÷365	$H_2CO \rightarrow H_2 + CO$	0.5÷0.6 [4]
	300÷330	$H_2CO \rightarrow H + HCO$	0.3÷0.5 [4]
NO_2	368	$NO_2 \rightarrow NO + O(^3P)$	~1 (λ = 313 nm)
HONO	370	$HONO \rightarrow OH + NO$	~1
HNO_3	300	$HNO_3 \rightarrow OH + NO_2$	~1
H_2O_2	254	$H_2O_2 \rightarrow 2OH$	~1

The situation is similar with nitric acid, hydrogen peroxide, and formaldehyde. The photodissociation of NO_2 cannot likewise result in a rapid transformation of impurities, since the former process involves the formation of an oxygen atom in the ground state $O(^3P)$. In the atmospheric conditions with a high content of oxygen, this atom reacts almost immediately with O_2 to form ozone.

The photolysis of ozone occurs in two ways. In the long-wavelength region ($\lambda > 320$ nm), photolysis brings about the formation of an oxygen atom in the ground state, $O(^3P)$, whereas at shorter wavelengths an oxygen atom in the excited state, $O(^1D)$, is formed. A feature of this atom is that it can react with water molecules, yielding two OH radicals:

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

It is these reactions, resulting in the formation of OH radicals, that are responsible for nearly all the variety of chemical processes in the troposphere. It is worth noting that ozone enters the troposphere from the stratosphere,[1] although in the event of a high level of atmospheric pollution, one should take account of ozone sources within the troposphere.

Fig. 2 presents a scheme illustrating the general character of the chemical reactions involved. Its most characteristic feature is the occurrence of chain reactions of the type $OH \rightarrow HO_2 \rightarrow OH$. However, the chain lengths are short, being no more than several units in the layer adjacent to the surface of the Earth. Another peculiarity resides in the fact that the initial transformations of stable impurity components begin with reactions involving the OH radical. For example, the transformation of methane in the atmosphere begins with the reaction

$$OH + CH_4 \rightarrow CH_3 + H_2O,$$

followed by the reactions

$$CH_3 + O_2 \rightarrow CH_3O_2,$$

$$CH_3O_2 + NO \rightarrow NO_2 + CH_3O,$$

$$CH_3O + O_2 \rightarrow HO_2 + CH_2O,$$

$$NO_2 \xrightarrow{h\nu} NO + O,$$

$$O + O_2 \rightarrow O_3 \text{ etc.}$$

This means that substances incapable of reacting with the OH radical will have very long lifetimes, as found in the case of freons.

To describe the scheme presented in Fig. 2, one should consider approximately 40 reactions. The question is therefore often asked whether the number of reactions that need to be considered could be made smaller. As previously mentioned, the key species responsible for the transformations in the troposphere is the OH radical. The above question may be therefore worded as follows: let us assume that a reaction is important if a change in its rate by a factor of 2 results in a change in the hydroxyl concentration of 10% or more. In this case we would need to consider only 10 reactions. If the same assumption is made also to apply to all the intermediate radical species, one should consider 24 reactions.

Hence it is impossible to reduce substantially the number of reactions that need to be taken into account without a loss in the accuracy of description. It is worth noting that the validity of the kinetic description is supported by the fact that calculated concentrations of different substances agree fairly well with those obtained experimentally.[5] This allows us to formulate and solve the more complicated problem, namely simultaneous description of the processes of the transport and transformation of impurities.

2. Mathematical model of the transport and transformation of impurities

To describe the processes of the transport of impurities that would take account of chemical reactions we need mathematical models that will adequately reproduce from the physical viewpoint the motion of the atmosphere over the Earth's nonuniform surface, redistribution of various pollutants in the lower layers of the atmosphere, their transport to the upper levels, and incorporation into the system of atmospheric circulation.

One of the main 'blocks' of mathematical models developed for the solution of environmental problems is that describing the processes of the transformation of impurities. The design of such a block is governed by the fact that the atmosphere of each industrial region or city is characterised by a specific assortment of substances of natural and anthropogenic origin which may interact with each other and undergo transformations. Therefore the block describing the transformation of impurities should be specially adapted to fit the environmental conditions of the sites under investigation.

Atmospheric impurities form a multicomponent medium. The different components interact with the atmosphere and with each other. Depending on the specific physical formulation of a problem and the objectives pursued, one may describe the transformation of substances with different degrees of detail. In doing so, the 'lifetime' of each substance may be regarded as its prime characteristic. However, prior to incorporating the model of reactions into the equation of the transport of impurities, this model should be adjusted so that it does not disturb the main equilibrium conditions with respect to the mass yield of substances.

Simulation of chemical processes in the atmosphere has special features of its own. Systems of differential equations describing

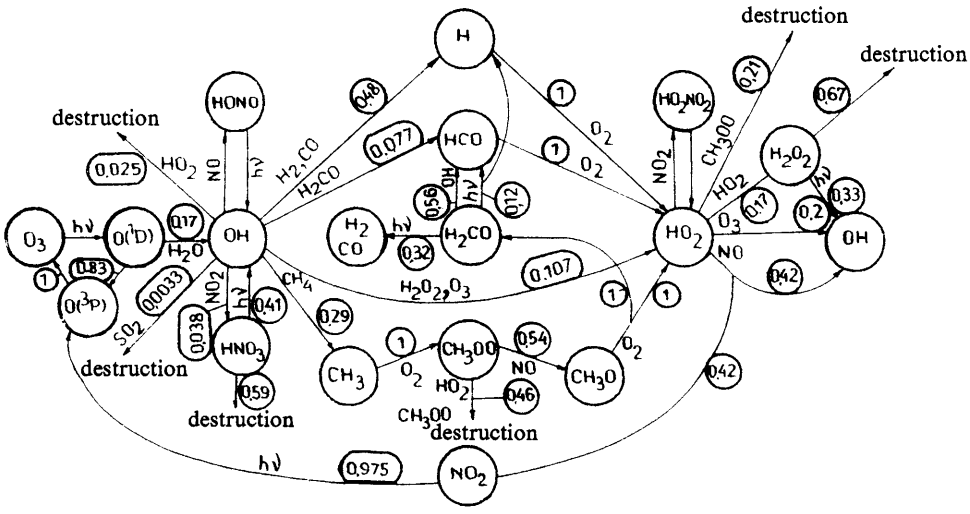


Figure 2. Scheme of chemical processes in the atmospheric layer close to the surface of the Earth; the numbers give the probability of the occurrence of particular reactions.

these processes are nonlinear. In actual problems, the number of reactions may be as great as several hundred, these reactions occurring throughout a three-dimensional domain comparatively large in size, since a typical size of an industrial region is about 100 km. Reaction rate constants differ from one another by orders of magnitude, their true values being not always precisely known. On the basis of their properties, the systems of differential equations which define the impurity transformation block may be classed as 'rigid' ones, characterised by a wide range of points within a spectrum of matrices of linearised equations. At each point of the three-dimensional space there may exist specific rigidity constraints, imposed on the system of equations, while the characteristic time scales involved in the description of chemical reactions should fit those of hydrometeorological processes. All this defines the main requirements that must be satisfied by mathematical models of the processes under study and methods of their computer-aided implementation.

The general structure of models and methods for the solution of a given class of problems, as well as examples of how to use them under specific conditions, are presented in Warneek's monograph.[6] In this paper we have therefore restricted ourselves to a brief account of the main stages of modelling.

As an example, let us consider the model of the transport and diffusion of an impurity in the atmosphere of an industrial region, these processes occurring against the background of local atmospheric events. We shall assume that all the required parameters of meteorological fields and their turbulence characteristics are given. These parameters are determined either through the use of hydrodynamic models or by measuring them in a real atmospheric environment.

Let us designate the domain as $D_t = D[0, \bar{t}]$, where D is the range of variation of spatial coordinates (x, y, z); $[0, \bar{t}]$ is the interval of time t, x and y are the coordinates in the horizontal plane and z is the altitude.

Let there be n gaseous impurities with concentrations

$$c_i = c_i(\vec{x}, t), \quad \vec{x} = (x, y, z), \quad (i = \overline{1, n}).$$

Let us designate the vector composed from these concentrations as

$$\vec{c} = \{c_i\} \quad (i = \overline{1, n})$$

and use the following system of equations to describe the processes of the transport and transformation of impurities:

$$\frac{\partial c_i}{\partial t} + \operatorname{div} \vec{u} c_i - \frac{\partial}{\partial x} \mu_x \frac{\partial c_i}{\partial x} - \frac{\partial}{\partial y} \mu_y \frac{\partial c_i}{\partial y} - \frac{\partial}{\partial z} \nu_z \frac{\partial c_i}{\partial z} +$$

$$+ B_i(\vec{c}, \theta) = F_i \quad (i = \overline{1, n}) \tag{1}$$

where

$$\operatorname{div} \vec{u} c_i \equiv \frac{\partial u c_i}{\partial x} + \frac{\partial v c_i}{\partial y} + \frac{\partial w c_i}{\partial z}; \quad \vec{F} \equiv \{F_i\} \quad (i = \overline{1, n})$$

are the sources of the impurities; $\vec{u} = (u, v, w)$ is the velocity vector; μ_x, μ_y and ν_z are respectively the coefficients of turbulent exchange of impurities in the directions x, y, and z, and θ is the air temperature. Judging by their structure, these coefficients are diagonal matrices of an order n, defined throughout the domain D_t. The coefficients of molecular diffusion are incorporated in ν_x, μ_y, and ν_z In principle, the effect of molecular diffusion may be neglected everywhere outside the lowest atmospheric layers adjacent to surface roughness. The rates of gravitational sinking or rise of impurities $w_g = \{w_i\}$ $(i = \overline{1, n})$ are incorporated in the vertical component w of the velocity vector $\boldsymbol{u}$. A matrix operator

$$B_i(\vec{c}, \theta) \equiv \{B_{ij}(\vec{x}, t, \vec{c}, \theta)\} \quad (i, j = \overline{1, n}) \tag{2}$$

defines the rates of change of the concentrations of impurities due to their transformation. Chemical reactions are nonlinear, i.e. the elements of an operator depend not only on the spatial coordinates and time, but also on the concentrations of the impurities themselves and the temperature.

A mathematical model deals with averaged fields of hydrometeorological parameters and concentrations of impurities. The scale of averaging depends on the procedure for the sampling of a model; in finite difference models this scale is characterised by the sizes of space–time cells of the lattice domain $D_t^n c D_t$. This should be taken into consideration when calculating the rates of transformation of impurities. It may be formally done through determining the average transformation rates from the average concentrations, using the same scale of averaging as that adopted in the sampling of the model. Such parametrisation procedure follows from the basic correlations of the balance of substances. Naturally, when this procedure is used, additional requirements are imposed on the choice of steps for the sampling of the model.

For the sake of simplicity, assume that contaminants do not directly influence the dynamics of the atmosphere. This assumption enables the transport and transformation processes to be considered against the background of motion of the atmosphere, the feedback from hydrothermodynamic processes being effected only through the flows of heat and moisture, and the radiation characteristics of the atmosphere.

The boundary conditions at the upper and lateral boundaries of a domain are set in such a way that the concentrations of impurities fit their background values. At the lower boundary, this condition is written in a parametric form, starting with the equation of the balance of impurities at the surface roughness level. Assuming that each impurity interacts independently with the surface of the Earth, we get

$$v_z \frac{\partial c_i}{\partial z} + \tilde{w}_i c_i = \beta_i c_i + f_{si} \quad (i = \overline{1, n}), \tag{3}$$

where β_i describes the interaction of an impurity i with the underlying surface, and f_{si} is the source of this impurity at the Earth's surface.

Different ways of parametrisation of the boundary conditions at the lower boundary of the air mass are used,[6] depending on the specific formulation of the problem.

At the initial moment, $t = 0$, the concentrations of impurities in the domain D are assumed to be known. The algorithm adopted for the solution of problems (1)–(3), is based on the splitting method. This leads to an effective and simple implementation of the model on a computer.

One usually distinguishes two stages of splitting of the equation system. The first describes the transport of impurities along the trajectories of air masses defined by the field of wind velocity $\vec{u}$, and their exchange through turbulence; the second describes the local conversions of impurities through transformation processes and takes account of their sources.

The computing algorithm is organised in such a way that, in the first stage, the equations of transport and turbulent diffusion are solved with respect to the concentrations c_i ($i = \overline{1, n}$) of each substance and independently of the others within the domain D^n and time interval $t_j \leqslant t \leqslant t_{j+1}$ with duration Δt. In the second stage, the mutual adaptation and interaction of all substances are accomplished at every point within the domain D^n independently from other points.

In practical calculations, the equation system describing the transformation of impurities need not be solved at every lattice point of the domain D^n, but only at those points where impurity concentrations reach certain threshold values, at which it becomes worthwhile to consider transformation processes. Confinement of the transformation of impurities to particular cells of the lattice domain D^n, which is a characteristic feature of the splitting method, is quite consistent with the short characteristic times of chemical reactions. Hence taking account of the transformation of impurities at an individual stage of splitting is one way of its parametrisation in numerical models. In this approach it is essential that changes in the description of particular reactions or of the mechanism of the transport of impurities as a whole are introduced at the level of separate blocks and do not affect the overall structure of the mathematical model.

The main principles of the design and implementation of models of the chemical transformation of impurities, were developed by simulating emissions which are most typical of the atmosphere of industrial cities: the emissions of sulphur-containing substances, nitrogen oxides and methane (as an illustration of the possible mechanisms of photochemical oxidiation of hydrocarbons). These individual types of transformations may occur in different combinations, depending on specific chemical conditions in the atmosphere of an industrial region. They have been incorporated in mathematical models of hydrometeorological processes and atmospheric pollution. Altogether up to 200 chemical reactions, involving 32 chemical species with different lifetimes, were included. These models were used to carry out a series of numerical trials covering a fairly wide range of possible emissions. Examples of these calculations have been reported earlier.[6–8] A model of the transport of impurities that took no account of transformation processes was also used in evaluating the impact of different anthropogenic sources of pollution on the Baikal lake area. From the analysis of results of the calculations conclusions were made as to the relative hazard to Baikal of sources located both in the lake area itself, and at greater distances in the Northern hemisphere.

Numerical trials performed with the aid of the models have demonstrated the advantages of a combined study of the conditions leading to the setting up of a hydrometeorological regime and the transport and transformation of impurities; this basic procedure makes it easier to take account of direct relations and feedbacks when estimating the influence of various natural and anthropogenic factors on the environment.

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Translated from *Uspekhi Khimii* **60** 521–529 (1991)

Transformation of nitrogen- and sulphur-containing compounds in the atmosphere and procedures for reducing the amounts of nitrogen and sulphur oxides in industrial waste

O M Sarkisov
Institute of Chemical Physics, USSR Academy of Sciences, Moscow

Various nitrogen- and sulphur-containing compounds of both natural and anthropogenic origin enter the atmosphere of our planet. Examples of compounds of natural origin are reduced sulphur compounds [H_2S, CS_2, $(CH_3)_2S$, COS] and nitrogen-containing compounds (NH_3, N_2O). The principal sources of nitrogen- and sulphur-containing compounds of anthropogenic origin are nitrogen and sulphur oxides.

Various aspects of the protection of the air on our planet and in the first place the problem of "acid rain" require the knowledge of the mechanisms of the chemical transformations of nitrogen- and sulphur-containing compounds in the atmosphere. It is known that the appearance of "acid" rain may be caused by the increased content in the troposphere of the oxides NO_x and SO_2. The knowledge of the mechanisms of the formation and removal of NO_x and SO_2 from the troposphere is therefore essential. The understanding of the principles governing the self-purification of the tropsphere makes it possible to employ them for the creation of technological processes leading to a decrease in the anthropogenic NO_x and SO_2 waste ejected into the atmosphere.

The gas-phase processes relevant to the problem under consideration have been investigated for several years at the Institute of Chemical Physics of the USSR Academy of Sciences. Problems of practical importance are solved jointly with other organisations. For example, the solution of the problem of the influence of photochemical sources of sulphur and nitrogen compounds on the background level of air pollution on a regional and global scale is being sought jointly with the Laboratory for Atmospheric Monitoring. The development of methods for the purification of industrial gaseous waste is being prosecuted together with the Dzerzhinskii All-Union Thermotechnical Institute (VTI), the Southern Branch of the VTI (YuzhVTI), and the Krzhizhanovskii Energy Institute (ENIN).

Consistent study of the elementary reactions, on the basis of which the mechanisms of the chemical transformation of particular compounds in the atmosphere were devised, served as the starting point for the research being prosecuted. These studies have made a definite contribution to the understanding of the mechanisms of the oxidation of hydrogen sulphide, carbon disulphide, and ammonia in the atmosphere which has been achieved and have made it possible to propose physicochemical models for the technological developments designed to reduce the nitrogen and sulphur oxide waste ejected into the atmosphere.

Table 1. Examples of the elementary processes investigated.

(a) Reactions of radicals with components of the atmosphere (R + M → products)

R	M	Refs.
NH_2	O_2, NO, NO_2, O_3, SO_2	[1–5]
HNO	NO, HNO	[6]
OH	NH_3, CS_2	[7, 8]
HS	O_2, NO_2	[9]
HSO	NO_2, NO	[9, 10]
HO_2	NO, H_2S, HO_2, NH_2, HNO	[11, 12]

(b) Heterogeneous radical destruction processes (R + surface → destruction)

R	Surface	Refs.
HO_2	Teflon, quartz, boric acid, metal oxides, NaCl, etc.	[13, 14]
OH	Quartz, sulphuric acid, Teflon, boric acid, ice, etc.	[15]
NH_2	Quartz, quartz coated by adsorbed NH_3	[16]

(c) Elementary processes with participation of excited species ($A^* + M \rightarrow$ products, $A^* + M \rightarrow A + M$)

A*	M	Refs.
$O(^1D)$	NH_3, H_2, CH_4, O_3	[17, 18]
$NH_2(v)$	O_2, N_2, O_3, CH_4	[19]
$NO_2(v)$	NO_2, CO	[20]
$OH(v)$	N_2, O_2, O_3, CH_4, H_2	[18, 21]
$O_3(v)$	O	[22]

The majority of the gas-phase reactions in the atmosphere involve the participation of radicals. For this reason, three types of elementary processes were investigated: the reactions of radicals with the components of the atmosphere; the radical-destruction reactions on surfaces close in chemical composition to that of aerosols; elementary processes with participation of excited species (Table 1). The present day requirements are such that virtually only studies of elementary processes by direct spectroscopic methods are of practical value. For this reason, we developed new effective methods for the investigation of elementary processes based on advances in laser and computer techniques.[23]