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USE OF A MATHEMATICAL MODEL FOR ANALYSIS OF SMALL GASES IN THE SURFACE LAYER OF THE ATMOSPHERE

Abstract. *The creation of a model for calculating and analyzing small gases is an urgent task in modern science and practice. The proposed model for calculating the concentration of tropospheric gases makes it possible to calculate the change in the values of seven chemical elements depending on the initial value of nitrogen oxide, nitrogen dioxide and carbon monoxide. The results of the comparative analysis show that the proposed model of tropospheric chemistry with the initial data, reaction rate constants and values of the drop and loss, basically, adequately describes the photochemical processes occurring in the near-surface urban (Tashkent) layer.*

The performed quantitative estimates of the accuracy of the model in comparison with the observed data showed, within the acceptable error, that the values of ozone and carbon monoxide calculated by the model do not coincide in percentage relative to the absolute values by 7.1% and 2%. In the future, it is necessary, on the basis of numerical experiments, for example, by iteration methods, to optimize the coefficients for small gases, which are of anthropogenic nature.

Key words: *small gases in the atmosphere, ozone, carbon monoxide, tropospheric chemistry model.*

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ИСПОЛЬЗОВАНИЕ МАТЕМАТИЧЕСКОЙ МОДЕЛИ ДЛЯ АНАЛИЗА МАЛЫХ ГАЗОВ В ПРИЗЕМНОМ СЛОЕ АТМОСФЕРЫ

Аннотация. *Создание модели для расчёта и анализа малых газов является актуальной задачей в современной науке и практике. Предлагаемая модель для расчёта концентрации тропосферных газов дает возможность рассчитывать изменение значений семи химических элементов в зависимости от начального значения оксида азота, диоксида азота и оксида углерода. Результаты сравнительного анализа показывают, что предложенная модель химии тропосферы с исходными данными, константами скорости реакции и значениями перепада и потерь, в основном, адекватно описывает фотохимические процессы, происходящие в приповерхностном городском (Ташкент) слое.*

Выполненные количественные оценки точности работы модели в сравнении с наблюдёнными данными показали в пределах допустимой ошибки, что значения озона и окиси углерода, рассчитанные по модели, не совпадают в процентах относительно абсолютных значений на 7,1% и 2%. В дальнейшем необходимо на основании численных экспериментов, например, методами итераций, выполнить оптимизацию коэффициентов для малых газов, имеющие антропогенную природу..

Ключевые слова: *малые газы в атмосфере, озон, оксид углерода, модель тропосферной химии.*

Introduction and problem statement. The composition of dry air is 99% nitrogen and oxygen. Only 1% are all other (minor) gases. And also in the atmosphere there is always a large amount of suspended solid and liquid particles (aerosol).

Due to various chemical reactions and dynamic processes in the atmosphere, the formation and disappearance of small gases constantly occurs. In fig. 1. the main processes

are shown in schematic form [6], determining the dynamics of the gaseous components of the atmosphere. Despite the low concentration of gases, they play an extremely important role in the thermodynamic processes of the atmosphere, the water cycle in the atmosphere, etc.

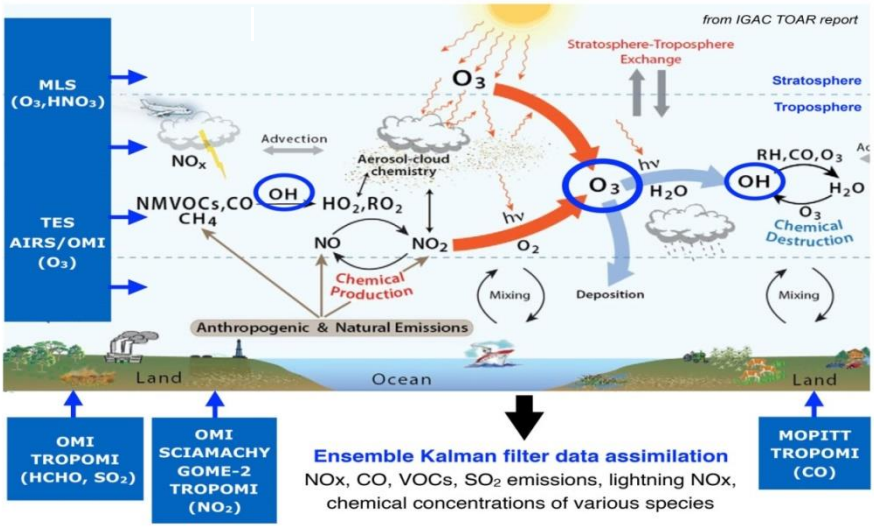

Fig. 1. Basic chemical processes in the troposphere and instruments for detecting small gases [3]

The need to diagnose and predict the concentration of gas components in the atmosphere is very relevant because their growth above the maximum permissible concentrations negatively affects the state of the environment and is dangerous to human health [2].

Study of the problem. In the work [14], a method was developed for calculating and criteria for the equilibrium, vibrational and chaotic behavior of a nonlinear model of tropospheric gases, which includes the chemical reactions of seven elements: CO, CO2, O3, NO, NO2, HO, HO2, CH4.

Further studies of the model showed that the intensity and speed of reactions in different physical and geographical conditions are different. Therefore, the use of the model in a practical application requires for a specific geographic area to adapt the model taking into account the features of this area, i.e. performing the procedure for recalculating the coefficients included in the model, as suggested in [12]. In this work, the coefficients were corrected based on numerical experiments.

The aim and objectives of the work. Taking into account the above, we propose for the analysis of small gases to use a mathematical model developed on the basis of fundamental gas laws and chemical reactions arising from them [3]. The object of the research is the mathematical model developed by us, and the purpose of the research is to adapt the fundamental, theoretical model for solving practical problems.

Materials and methods. Determination of model coefficients based on fundamental research. The model is based on the following chemical reactions:

1) The formation of an oxygen atom $O(^3P)$ during the photolysis of nitrogen dioxide (NO_2) is a fundamental reaction that causes the direct formation of O_3 in the troposphere. Under the influence of the solar flux reaching the troposphere, as a result of photodissociation, the following process occurs [1]:

$$NO_2 + h\nu + O_2 \rightarrow NO + O_3 \quad (1)$$

Rate constants at 298 K and Arrhenius parameters for chemical reactions:

k_{R2} (298 K) = $1,6 \cdot 10^{-14}$ $sm^3 \cdot molecule^{-1} \cdot sec^{-1}$ in M=$2,69 \cdot 10^{29}$ $sm^3 \cdot molecule^{-1} \cdot sec^{-1}$

$$k_{R2} (T) = k_0 (T/300)^{-2,6} sm^3 \cdot molecule^{-1} \cdot sec^{-1}.$$

2) The reaction of OH and O_3 radicals is an important reaction that converts OH to HO_2 in the HO_X cycle in the process of ozone dissociation in the lower stratosphere and upper troposphere. In the troposphere, HO_2 is also reproduced through the OH + CO reaction even in a clean atmosphere [2].

The reaction of OH and O_3 proceeds with the formation of a radical HO_2 [1]:

$$OH + O_3 \rightarrow HO_2 + O_2 \quad (2)$$

The IUPAC Subcommittee recommends the rate constant of this reaction at 298 K and the temperature dependence take as:

k_{R3} (298 K) = $7,3 \cdot 10^{-14}$ $sm^3 \cdot molecule^{-1} \cdot sec^{-1}$,

$k_{R3} (T) = 1,7 \cdot 10^{-12} \cdot \exp(-940/T)$ $sm^3 \cdot molecule^{-1} \cdot sec^{-1}$.

3) The reaction of OH and CO is important for the OH radical as the main reaction in the pure troposphere, as well as for CO to determine its atmospheric lifetime. In many works, the rate constants of this reaction were refined, in particular, in [1] it was obtained:

$$OH + CO + O_2 \rightarrow HO_2 + CO_2. \quad (3)$$

For the reaction under consideration, the reaction rate constant at 298 K and the temperature dependence are written in the form:

k_{R4} (298 K) ~ $1,5 \cdot 10^{-12}$ $sm^3 \cdot molecule^{-1} \cdot sec^{-1}$,

$k_{R4} (T) = 1,1 \cdot 10^{-12} \cdot (T/300)^{-1,3}$ $sm^3 \cdot molecule^{-1} \cdot sec^{-1}$.

4) OH radicals react with all alkanes. Consider methane (CH_4) as a typical alkane. Since the lifetime of alkanes in the atmosphere is determined by the rate of reaction with OH, for example, the exact rate constant of OH + CH_4 is important for assessing global warming [4].

OH reactions with alkanes represent an abstraction of the H-atom, such as [1]:

$$CH_4 + OH + 2O_2 \rightarrow CO + HO_2 + 2H_2O \quad (4)$$

For this reaction coefficients:

k_{R6} (298 K) = $6,4 \cdot 10^{-15}$ $sm^3 \cdot molecule^{-1} \cdot sec^{-1}$,

and the dependence on temperature as,

$k_{R6} (T) = 1,85 \cdot 10^{-12} \cdot \exp(-1690/T)$ $sm^3 \cdot molecule^{-1} \cdot sec^{-1}$

5) The reaction of HO_2 and NO with the formation of OH and NO_2 is an important reaction for the completion of the OH–HO_2 chain reaction in the troposphere and stratosphere [5]. Particularly in the troposphere, it is a fundamental reaction for the production of photochemical ozone along with the reaction of RO_2 and NO.

$$HO_2 + NO \rightarrow HO + NO_2 \quad (5)$$

Rate constant and temperature dependence of the reaction rate:

k_{R8} (298 K) = $8,0 \cdot 10^{-12}$ $sm^3 \cdot molecule^{-1} \cdot sec^{-1}$,

$k_{R8} (T) = 3,3 \cdot 10^{-12} \cdot \exp(270/T)$ $sm^3 \cdot molecule^{-1} \cdot sec^{-1}$;

6) The reaction of O_3 and NO in the troposphere temporarily dissipates O_3 and is known as the "titration reaction" [7], which is important for the nearest sources of NO_x and in urban air [2].

The reaction of O_3 and NO can be written as [1]:

$$O_3 + NO \rightarrow NO_2 + O_2 \quad (6)$$

Recommended values of rate constants for this reaction:

k_{R10} (298 K) = $sm^3 \cdot molecule^{-1} \cdot sec^{-1}$,

Arrhenius formula in the temperature range 195-308 K

$k_{R10} (T) = 1,4 \cdot 10^{-12} \cdot \exp(-1310/T)$ $sm^3 \cdot molecule^{-1} \cdot sec^{-1}$.

The model also includes the values of physical sources (CO, NO, NO_2 and O_3) and losses (NO, NO_2 and O_3) [8].

Based on all the above reactions, we will compose a system of equations:

$$\left.\begin{aligned}
&\frac{d[CO]}{dt} = k_{R6}[CH_4][OH] - k_{R4}[CO][OH] + F_{CO},\\
&\frac{d[O_3]}{dt} = k_{R2}[NO_2] - k_{R1}[O_3] - k_{R7}[HO_2][O_3] - k_{R10}[NO][O_3] - k_{R3}[OH][O_3] -\\
&L_{O3}[O_3] + F_{O3},\\
&\frac{d[NO]}{dt} = k_{R2}[NO_2] - k_{R10}[NO][O_3] - k_{R8}[HO_2][NO] - L_{NO}[NO] + F_{NO},\\
&\frac{d[NO_2]}{dt} = k_{R10}[NO][O_3] + k_{R8}[HO_2][NO] - k_{R2}[NO_2] - k_{R5}[HO][NO_2] - L_{NO2}[NO_2],\\
&\frac{d[HO]}{dt} = 2k_{R1}[O_3] + k_{R7}[HO_2][O_3] + k_{R8}[HO_2][NO] - k_{R4}[OH][CO] -\\
&k_{R5}[OH][NO_2] - k_{R3}[OH][O_3] - k_{R6}[CH_4][OH],\\
&\frac{d[HO_2]}{dt} = k_{R4}[OH][CO] + k_{R3}[OH][O_3] + 2k_{R6}[CH_4][OH] - k_{R7}[HO_2][O_3] -\\
&k_{R8}[HO_2][NO] - k_{R9}[HO_2][HO_2],\\
&\frac{d[CH_4]}{dt} = -k_{R6}[CH_4][OH].
\end{aligned}\right\} \quad (7)$$

Results of Research. To assess the adequacy of the proposed tropospheric chemistry model and the methodology for its calculation, numerical calculations of the model were carried out under the following initial conditions and reaction rate constants [15]:

$u_0 = 5.89 \cdot 10^{11}$ molecule/sm^3; $v_0 = 3.9 \cdot 10^{11}$ molecule/sm^3;
$x_0 = 3.928 \cdot 10^9$ molecule/sm^3; $w_0 = 3.043 \cdot 10^9$ molecule/sm^3;
$y_0 = 0.825 \cdot 10^7$ molecule/sm^3; $z_0 = 0.05 \cdot 10^9$ molecule/smmolecule/sm^3;
$s_0 = 4.2 \cdot 10^{13}$ molecule/sm^3,
$k_{R1} = 4.7 \cdot 10^{-10}$ c^{-1}; $k_{R2} = 3.9 \cdot 10^{-4}$ c^{-1}; $k_{R3} = 7.3 \cdot 10^{-14}$ sm$^3 \cdot$molecule$^{-1} \cdot$sec^{-1};
$k_{R4} = 1.5 \cdot 10^{-12}$ sm$^3 \cdot$molecule$^{-1} \cdot$sec^{-1}; $k_{R5} = 1.1 \cdot 10^{-11}$ sm$^3 \cdot$molecule$^{-1} \cdot$sec^{-1};
$k_{R6} = 6.4 \cdot 10^{-15}$ sm$^3 \cdot$molecule$^{-1} \cdot$sec^{-1}; $k_{R7} = 1.9 \cdot 10^{-15}$ sm$^3 \cdot$molecule$^{-1} \cdot$sec^{-1};
$k_{R8} = 8.0 \cdot 10^{-12}$ sm$^3 \cdot$molecule$^{-1} \cdot$sec^{-1}; $k_{R9} = 1.4 \cdot 10^{-10}$ sm$^3 \cdot$molecule$^{-1} \cdot$sec^{-1};
$k_{R10} = 1.8 \cdot 10^{-14}$ sm$^3 \cdot$molecule$^{-1} \cdot$secsm$^3 \cdot$molecule$^{-1} \cdot$sec^{-1}.
Inflow and loss accepted:
$F_{CO} = 9.5 \cdot 10^4$ molecule sm^{-3} sec^{-1}; $F_{O3} = 6.0 \cdot 10^4$ molecule sm^{-3} sec^{-1};
$F_{NO} = 1.0 \cdot 10^3$ molecule sm^{-3} sec^{-1}; $L_{O3} = 9.6 \cdot 10^{-12}$ molecule sm^{-3} sec^{-1};
$L_{NO} = 1.9 \cdot 10^{-8}$ molecule sm^{-3} sec^{-1}; $L_{NO2} = 7.2 \cdot 10^{-8}$ molecule sm^{-3} sec^{-1}.

The solution of model (7) by the Runge-Kutta method [10, 11, 13] are shown in Fig. 2. Analysis of the graphs shows that with the accepted initial data and coefficients of inflow and runoff, the values of ground-level ozone are $8{,}8 \cdot 10^{11}$ molecule sm^{-3} or 32,7 ppb. The annual average value of ground-level ozone according to the measurements of Uzhydromet is 35.2 ppb.

In this case, the value of CO was $21{,}1 \cdot 10^{11}$ molecule sm^{-3} or 78,4 ppb.

Let us compare the obtained model data with the measurement data of Uzhydromet. Average value for CO according to Uzhydromet were 80 ppb. The difference between measure and the calculated values is 1,6 ppb, which in percentages relative to absolute values corresponds to 2%.

Thus, for ground-level ozone and carbon monoxide, the difference between the measurement data of Uzhydromet and the mathematical model is small, and for nitrogen oxides it is quite large. This is due to the fact that, for objective reasons, the model does not take into account emissions of gases of an anthropogenic nature (emissions of gases from vehicles, thermal power plants, etc.). In addition, the presented model does not take into account the reaction rate as a function of temperature. Here the task is to keep the main

reactions of formation and transformation of oxides given in this model and take into account the dependence of the reaction rate on temperature. The solution to this problem requires further development of the model (which is currently being worked on), as well as the use in the model of a higher temporal resolution of data (for example, not monthly average, but daily average).

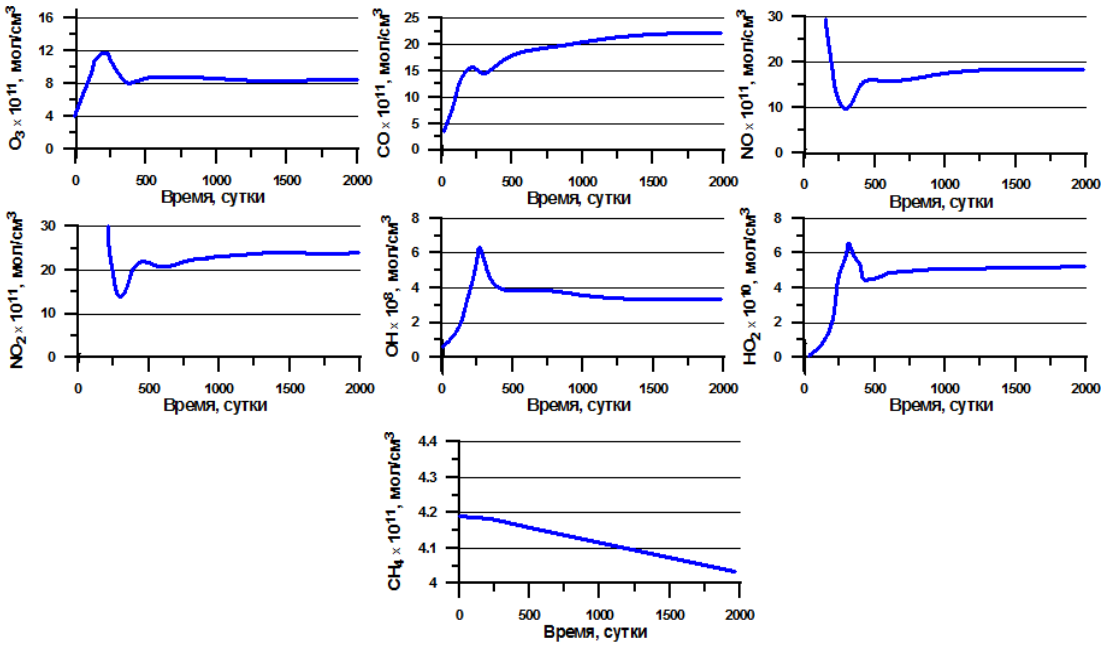

Fig. 2. Changes in the concentration of O_3, CO, NO, NO_2, OH, HO_2 and CH_4 as a function of time

Conclusion. The proposed tropospheric chemistry model with the accepted initial data, reaction rate constants, and inflow and runoff values as a whole adequately describes the photochemical processes occurring in the surface urban (Tashkent) layer. Ground-level ozone and carbon monoxide deviate by 7.1% and 2% is unsatisfactory.

The developed method for calculating a system of nonlinear differential equations for the concentration of tropospheric gases allows setting the parameters of the initial concentration of tropospheric gases, calculating the eigenvalues of the matrix of the system of equations, choosing the values of the variable quantity of nitric oxide and carbon monoxide, calculating the changes in the values of seven chemical elements depending on the influx of nitric oxide and oxide carbon.

Estimates of the model's accuracy showed that, firstly, this model of tropospheric chemistry adequately describes photochemical processes in the atmosphere with satisfactory values of small gases, except for nitrogen oxides, and, secondly, requires optimization with respect to the coefficients for small gases of nitrogen oxide due to unaccounted for in models of anthropogenic emissions and reaction rates as a function of temperature.

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