Journal of Applied Mechanics and Technical Physics, Vol. 37, No. 5, 1996

SOLUTION OF VARIATIONAL PROBLEMS OF GAS DYNAMICS WITH PHYSICOCHEMICAL TRANSFORMATIONS

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UDC 533.6.01

Many problems related to a moving gas with physicochemical transformations can be reduced to finding extreme values of functionals with respect to some sets of parameters determining the system. Such are the problems of finding the contour of a supersonic nozzle with maximum thrust, determining the body contour with minimum resistance to gas flow, problems of planning experiments aimed at obtaining reaction rate constants, etc. Any problem of purposeful planning, controlling or making necessary decision can be reduced to the problem of finding an extremum of a certain functional in the space of parameters.

Mathematically, such problems can be formulated as problems of nonlinear programming, which are solved, as a rule, by numerical methods.

1. A variational gas-dynamic problem related to determination of the optimum contour of a supersonic nozzle with allowance for physicochemical transformations is considered. As independent variables, we choose the Cartesian coordinate x along the nozzle axis and the flow function ψ in the form $d\psi = -\rho v y^r dx + \rho u y^r dy$ (y is the Cartesian coordinate perpendicular to the x axis).

The initial system of equations with allowance for vibrational relaxation processes and chemical reactions has the form [in a stationary formulation ignoring viscosity and heat conductivity (see, for example, [1])]

$$\frac{\partial y^{1+r}}{\partial \psi} = \frac{1+r}{\rho u}; \tag{1.1}$$

$$\frac{\partial (p y^{1+r})}{\partial \psi} = \frac{(1+r)p}{\rho u} - y\frac{\partial v}{\partial x}; \tag{1.2}$$

$$\frac{w\,\partial w}{\partial x} + \frac{1}{\rho}\frac{\partial p}{\partial x} = 0; \tag{1.3}$$

$$\frac{\partial c_i}{\partial x} = Z_i(e_j, c_k, u, p, T), \quad i = 1, \ldots, n; \quad j = 1, \ldots; k = 1, \ldots; \tag{1.4}$$

$$\frac{\partial e_i}{\partial x} = Q_i(e_j, c_k, u, p, T), \quad i = n+1, \ldots, n+nv; \quad j = 1, \ldots; k = 1, \ldots; \tag{1.5}$$

$$\frac{w^2}{2} + H = H_0; \tag{1.6}$$

$$p = \rho R_0 T \Sigma c_i; \tag{1.7}$$

$$\frac{\partial y}{\partial x} = \frac{v}{u}; \tag{1.8}$$

$$w^2 = u^2 + v^2. \tag{1.9}$$

Here, Eq. (1.1) is an implication of the continuity equation; (1.2) and (1.3) are the equations of motion; (1.4) is the equation of change in concentrations during chemical reactions; (1.5) is the equation of vibrational-energy

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Institute of Mechanics of the Moscow State University, Moscow 119899. Translated from Prikladnaya Mekhanika i Tekhnicheskaya Fizika, Vol. 37, No. 5, pp. 63–72, September–October, 1996. Original article submitted February 20, 1995; revision submitted June 28, 1995.

relaxation; (1.6) is the equation of energy; (1.7) is the equation of state; and (1.8) and (1.9) are the equations of the streamline y; u and v are the projections of the flow velocity w onto the axes of the rectangular Cartesian coordinate system; p, T, and ρ are the gas pressure, temperature, and density, respectively; R_0 is the universal gas constant; H and H_0 are the enthalpy of the unit mass of the gas at an arbitrary point and the stagnation enthalpy; e_i is the energy of the vibrational degrees of freedom; c_i are the mole-mass concentrations of the components [$c_i = N_i/(N_{\rm A}\rho)$, where N_i are the particle concentrations in cubic meters and $N_{\rm A}$ is the Avogadro number]; n is the number of chemical reactants; nv is the number of vibrational modes; and $r = 0$ and $r = 1$ denote the plane and axisymmetric gas flow, respectively.

Taking into account only the translational, rotational, and vibrational degrees of freedom of the gas and using a harmonic oscillator to model the vibrational mode, we can specify the system parameters as

$$e_i = 1/[\exp(\Theta_i/T_i) - 1], \quad H = \sum_{i=1}^{n} c_i h_i^0 + R_0 T \sum_{i=1}^{n} c_i(5/2 + r_i) + R_0 \sum_{i=n+1}^{n+nv} a_i \Theta_i c_{j(i)} e_i,$$

where h_i^0 is the enthalpy of formation of the ith particle; r_i is the number of rotational degrees of freedom of the ith particle; e_i is the vibrational energy of the ith mode per one molecule and one quantum; T_i and Θ_i are the vibrational and characteristic temperatures of the ith mode, respectively; a_i is the degeneracy factor of the ith vibrational mode; and $c_{j(i)}$ is the mole-mass fraction of the ith mode in the jth particle. The expression for enthalpy can also be written as

$$H = \sum_{i=1}^{n} c_i h_i^0 + \frac{R_0}{\mu T}\left(\frac{5}{2} + \sum_{i=1}^{n} \xi_i r_i\right) + \frac{R_0}{\mu} \sum_{i=n+1}^{n+nv} a_i \Theta_i \xi_{j(i)} e_i.$$

Here $1/\mu = \sum\limits_{k=1}^{n} c_k$; $\xi_i = c_i / \sum\limits_{k=1}^{n} c_k = c_i \mu$; μ is the molecular weight of the mixture; and ξ_i is the mole fraction of the ith component.

2. We assume that in a gas of n components m reactions of the following type can occur:

$$\sum_{i=1}^{n} \nu_{ij}^{+} Y_i \xrightarrow{K_j} \sum_{i=1}^{n} \nu_{ij}^{-} Y_i, \quad j = 1, 2, \ldots, m.$$

Here K_j is the rate constant of the direct reaction; ν_{ij}^{+} and ν_{ij}^{-} are stoichiometric coefficients; Y_i are the starting substances and the reaction products. The reverse reaction with rate constant K_{-j} can be written similarly. If the mole-mass concentrations c_i are used to define the concentration characteristic of the given substance, the phenomenological equations of chemical kinetics have the form

$$\frac{dc_i}{dt} = \frac{1}{\rho} \sum_{j=1}^{m} \beta_{ij} W_j = \frac{1}{\rho} \sum_{j=1}^{m} \beta_{ij} K_j \prod_{k=1}^{n} (\rho c_k)^{\nu_{jk}^{+}},$$

where $i = 1, 2, \ldots, n$; t is time; $\beta_{ij} = \nu_{ij}^{-} - \nu_{ij}^{+}$; ρ is the density of the gas mixture; K_j is the rate constant of the jth reaction; and W_j is the direct-reaction rate.

If one singles out terms that characterize the change in the amount of substances due to both the direct and reverse reactions, the latter equation takes the form

$$\frac{dc_i}{dt} = \frac{1}{\rho} \sum_{j} \beta_{ij} (W_j - W_{-j}),$$

where W_{-j} is the reverse-reaction rate, which can be written similarly to W_j.

The equations of relaxation for the vibrational energy of mode i, which is modeled by a harmonic oscillator, will be used under the following assumptions:

— the energy exchange inside each mode occurs much more rapidly than the intermode VV' exchange, vibrational-translational VT exchange, and chemical reactions;

— the rotational degrees of freedom are in equilibrium with the translational degrees of freedom;

— the Maxwell distribution in the translational degrees of freedom is preserved.

The system of relaxation equations for the vibrational energy is written for e_i (which is the average number of vibrational quanta of the ith type per one molecule) in the form [2]

$$\frac{de_i}{dt} = Q^i_{VT} + Q^i_{VV'} + Q^i_{CV}.$$

Here the term Q^i_{VT} takes into account the vibrational-translational VT exchange, $Q^i_{VV'}$ the intermode VV' exchange, and Q^i_{CV} the change in the vibrational energy due to chemical reactions involving vibrationally excited molecules (the CV process);

$$Q^i_{VT} = (e^0_i - e_i)/\tau_i; \quad \tau_i = \Big[\sum_{j=1}^{n} c_j/(\tau_{ij} \sum_k c_k)\Big]^{-1};$$

$$Q^i_{VV'} = k_{im}[e_m(e_i + 1)\exp(\Theta_m/T - \Theta_i/T) - (e_m + 1)e_i],$$

where e^0_i is the equilibrium value of the vibrational energy e_i at $T_i = T$; τ_{ij} is the time of vibrational relaxation of mode i upon collision with molecules of type j; k_{im} is the rate constant of VV' exchange between modes (molecules) i and m; Θ_i and Θ_m are the corresponding characteristic vibrational temperatures; and the expression $Q^i_{VV'}$ is written for a single-quantum exchange between molecules.

For the multi-quantum exchange, the form of $Q^i_{VV'}$ is somewhat more complex. Let in multi-quantum VV' exchange s quanta of mode i exchange with q quanta of mode m. Then the expression for $Q^i_{VV'}$ has the form [3]

$$Q^i_{VV'} = k_{im}(s/a_i)[e^q_m(e_i + 1)^s \exp(q\Theta_m/T - s\Theta_i/T) - (e_m + 1)^q e^s_i]$$

(a_i is the degeneracy factor of mode i). According to the principle of detailed balancing, the rate constant of the reverse process $k_{mi} = k_{im}\exp[(q\Theta_m - s\Theta_i)/T]$.

The change in the vibrational energy e_i of the ith type of oscillations in the jth molecule as a result of chemical reactions is taken into account by the term Q^i_{CV} in the form [2]

$$Q^i_{CV} = \frac{1}{\rho c_{j(i)}} \sum_{k=1}^{m} (\nu^-_{jk} - \nu^+_{jk})(e^*_{ik} - e_i)W_k,$$

where W_k is the rate of the kth chemical reaction; e^*_{ik} is the mean value of the vibrational energy lost (or gained) by the mode of type i in each act of the chemical reaction of type k.

A program for integrating Eqs. (1.1)–(1.9) for the flow of relaxing gas in the nozzle was designed. The program is universal, because the formation of the right-hand sides of kinetic equations (1.4) and (1.5) is based on the symbolic equation for reactions which are written as an ordinary molecular formula (for example, $O_2 + M \rightleftarrows O + O + M$). The terms Q^i_{VT}, $Q^i_{VV'}$, and Q^i_{CV}, which determine the change in vibrational energy e_i in VT, VV', and CV processes, are formed in a similar manner. A complete list of the processes along with data on the rate constants are stored as a separate data base. Thus, only the title of the data base is changed when one passes to another system of kinetic variables.

The program has a built-in editor for checking the base of physicochemical data in use. The editor checks whether the formulas of processes are recorded correctly. In particular, it picks the processes whose formulas contain elements that are not specified in the base of components. Also, the editor checks that the laws of conservation of mass or charge (for reactions involving charged particles) are satisfied for each reaction in the base. Such a routine check allows one to avoid occasional slips while forming the data base on a computer.

3. Suppose we need to determine a specific solution described by system (1.1)–(1.9) that is equivalent to finding an extremum of a functional $F(A_i)$ from the controlling parameters A_i under certain (in general, nonlinear) restrictions on the parameters A_i

$$g_m(A_i) = 0, \quad m = 1, 2, \ldots; \qquad g_k(A_i) \geqslant 0, \quad k = 1, 2, \ldots .$$

To find the model optimization parameters it is necessary to move to dimensionless variables in Eqs. (1.1)–(1.9), in the initial and boundary conditions, in the functional $F(A_i)$, and in the restrictions on the parameters A_i.

Analysis of the dimension of the problem shows that the flow field is determined by the following parameters: T_0, Π_i, ξ_i^0, a_k, y_0/L_0, and L/L_0. Here L_0 is the characteristic length of the problem; T_0 is the initial temperature ahead of the nozzle entry; ξ_i^0 are the initial concentrations of the components at point $x = x_0$ (e.g., the initial values of mole fractions); a_k are dimensionless parameters that determine the distribution of the dimensionless pressure $p/p_0 = p_1(x/L_0, a_k)$ along the nozzle axis; y_0 is the characteristic dimension along y; and Π_i are parameters that appear when one moves to dimensionless variables in kinetic Eqs. (1.4) and (1.5). If the nozzle length L is chosen as the characteristic length L_0, then $L/L_0 = 1$.

The solution of the problem in a one-dimensional formulation is independent of the parameter $d = y_0/L$. Such a dependence appears only when the process is two-dimensional.

The specific form of the parameters Π_i depends on the specific form of the kinetic equations. For the equations of VT and VV' relaxations, $\Pi_i = \Pi_1 = p_0 L_0$. For monomolecular reactions, $\Pi_1 = L_0$. For bimolecular reactions, $\Pi_1 = p_0 L_0$, and for trimolecular reactions, $\Pi_1 = p_0^2 L_0$. Thus, if the equations of vibrational relaxations (with allowance for VT and VV' processes) and(or) bimolecular reactions are used in calculations, the controlling parameter is the combination $p_0 L_0$ (i.e., the flow will be the same, if $\Pi_1 = p_0 L_0$ is conserved). If, in addition, one takes into account monomolecular and trimolecular reactions, the parameters p_0 and L_0 become the controlling parameters of optimization.

Sometimes, simultaneous allowance for monomolecular, bimolecular, and trimolecular reactions (along with reactions of higher order) can cause some mathematical difficulties in determining the actual optimum. This can be illustrated by the following example. Suppose that the initial system of kinetic equations is determined by bimolecular reactions. In this case, the complex $p_0 L_0$ is the optimization parameter. If an insignificant monomolecular reaction with a small reaction-rate constant is added to such a system, then, from a formal standpoint, we should consider two optimization parameters: p_0 and L_0, although the complex $\Pi_1 = p_0 L_0$ still remains the actual optimization parameter. In this case, if the tested functional has p_0 and L_0 among the parameters over which optimization is performed, its multidimensional hypersurface has an almost degenerate "gully" along the line $p_0 L_0 = \text{const}$, which complicates significantly the search for an optimum.

In this connection, it becomes important to choose the most essential physicochemical processes in solving variational problems of gas dynamics by direct methods [4]. On the one hand, the chosen leading processes make it possible to expedite flow-field calculations (to decrease computer time), and on the other hand, they contain the necessary structure of the types of reactions and processes that determine the set of optimization parameters.

As was been pointed out above, the full set of determining optimization parameters is found in moving to dimensionless parameters in the tested functional and restrictions on parameters.

4. Two problems are distinguished in the theory of the Laval nozzle: direct and inverse. The direct problem consists in finding the flow field for a given nozzle contour under certain conditions on the initial and final cross-sections of the nozzle. It can be reduced to a boundary-value problem for equations of gas dynamics. The inverse problem consists in determining the flow field under conditions specified on the known surface and conditions set on the initial cross-section of the nozzle. This problem can be reduced to a Cauchy problem. To find the flow field, let us solve the inverse problem of a Laval nozzle. In this case, the flow field in the region $G\{x_0 \leqslant x \leqslant x_k, \psi_0 \leqslant \psi \leqslant \psi_k\}$ can be found if, for example, the pressure distribution along the curve $\psi = \psi_0$ ($\psi_0 = 0$ on the axis) and the parameter values on the $x = x_0$ cross-section are specified. By using an appropriate finite-difference scheme, one can find the flow field in region G.

The general scheme of obtaining a numerical solution can be found, for instance, in [1]. We used it to calculate the gas flow field with physicochemical transformations in designing an optimal gas-dynamic ozone generator whose major unit was a supersonic Laval nozzle. The possibilities of such an ozonator were discussed in [5], where the optimum characteristics of the ozonator were obtained in a one-dimensional stationary formulation.

The basic design of the gas-dynamic ozonator is as follows. An oxygen-containing gas heated to temperature T_0 is forced with pressure p_0 through a supersonic nozzle. Upon cooling inside the nozzle, the O atoms that have formed by thermal dissociation of O_2 molecules at the nozzle inlet promote the formation of ozone molecules O_3 (primarily at the expense of the $O + O_2 + M \rightarrow O_3 + M$ reaction).

To increase the ozonator efficiency, it was assumed in [5] that an excess concentration of O atoms was created in a certain cross-section of the nozzle (for example, by an electric discharge). The optimum characteristics of this ozonator were determined in [5].

The actual two-dimensional character of the gas flow inside the nozzle can alter significantly some characteristics of this optimum ozonator. In this connection, we considered the problem of obtaining maximum concentrations of ozone O_3 with allowance for the two-dimensional character of the gas flow. The parametric distribution of the pressure p along the nozzle axis was specified as

$$p_1(x/L, a_k) = p/p_0 = (1+\beta)^{-1}[\exp(-\alpha(x/L)^{1+q}) + \beta] = p_1(x/L, \alpha, q, \beta),$$

where $\alpha > 0$, $q > 0$, and $\beta > 0$ are parameters that determine the pressure distribution ($a_1 = \alpha$, $a_2 = q$, and $a_3 = \beta$). The parameters have the following meaning. When $x \to L$ and the exponent tends to zero, the parameter β determines the degree of flow expansion on the axis, $p_1 \to \beta/(1+\beta)$, and the parameter α is the pressure gradient (and, hence, also the temperature gradient) in transition from the subsonic to the supersonic regime. The quantity q is an additional parameter for varying the pressure between 0 and L.

Next, it is assumed that additional O atoms appear in the plane $l = l(\psi)$ in region G under the following additional restrictions:

(a) O atoms are formed by dissociation of O_2 molecules, so that the following natural condition is satisfied on the jump surface $l = l(\psi)$: $z(O)_1 + z(O_2)_1 = z(O)_2 + z(O_2)_2$, $z(O)_2 > z(O)_1$, where $z(O)_1$, $z(O_2)_1$, $z(O)_2$, and $z(O_2)_2$ are the mass fractions of the components O and O_2 prior to and after the jump;

(b) the value of the jump $\Delta O = z(O)_2 - z(O)_1$ is the same over the entire plane $l(\psi)$;

(c) the heat Δq expended at the jump goes exclusively to dissociation of O_2 molecules, i.e., $\Delta q = \Delta c_1 h_1^0 + \Delta c_2 h_2^0 = \Delta c_1 h_1^0$ (c_1, c_2, h_1^0, and h_2^0 are the mole-mass concentrations and enthalpies of formation of O atoms and O_2 molecules respectively; by definition, $h_2^0 = 0$). In addition, it is assumed that the vibrational temperature T_V of molecular oxygen does not change during the jump. Values of the gas-dynamic parameters are found from ordinary relations for the jump (see [6], for example). It is easily seen that such a "kinetic" jump for small values of ΔO is a weak discontinuity surface of the gas-dynamic variables.

The following three parameters define the plane $l(\psi)$:

$$l(\psi)/L = (x_*/L)(1 + \gamma_1\psi + \gamma_2\psi^2) = x'_*(1 + \gamma'_1\psi' + \gamma'_2\psi'^2).$$

Here, $x'_* = x_*/L$, and ψ' is a normalized flow function: $\psi' = \psi/(\rho_0 u_0 L) = y_1/L$ and $y_1 = y|_{x=0}$. Thus, the optimization parameters for the mole fraction ξ_3 of ozone are as follows:

$$T_0,\ p_0,\ \xi_i^0,\ \alpha,\ q,\ \beta,\ L,\ x'_*,\ \gamma'_1,\ \gamma'_2,\ \Delta O,\ d. \tag{4.1}$$

In our case, p_0 and L are independent optimization parameters, inasmuch as the system takes into account essential bimolecular and trimolecular reactions $O+O_3 \rightleftarrows O_2+O_2$, $O+O_2+M \rightleftarrows O_3+M$, $O_2+M \rightleftarrows O+O+M$, and also the VT relaxation of the vibrational energy of oxygen $O_2(v)+M \to O_2+M$ (M is any of the particles).

The reaction rate constants entering in the generalized Arrhenius form $K = AT^n \exp(-E/T)$ (A, n, and E are parameters) and the accuracy of the suggested recommendation are given in [5]. The vibrational-translational relaxation of molecular oxygen has been widely studied. The VT relaxation times used here can be found in [7]. The calculations have shown that under the studied conditions the vibrational temperature of O_2 is close to the translational temperature. This is also confirmed by experiments on recombination of oxygen in nozzles [8].

Optimization over all parameters with the purpose of obtaining maximum values of the ozone concentration under the assumption of two-dimensional gas flow is time consuming. In this connection, the optimization problem was solved only for some parameters (4.1) that are of interest from the viewpoint of two-dimensionality of the gas flow. It is assumed that the equilibrium composition in the receiver is determined for the starting pure molecular oxygen O_2 at $T_0 = 1500$ K $p_0 = 20$ atm, and the optimum is sought for the parameters

$$\alpha,\ q,\ \beta,\ L,\ x'_*,\ \gamma'_1,\ \gamma'_2, \tag{4.2}$$

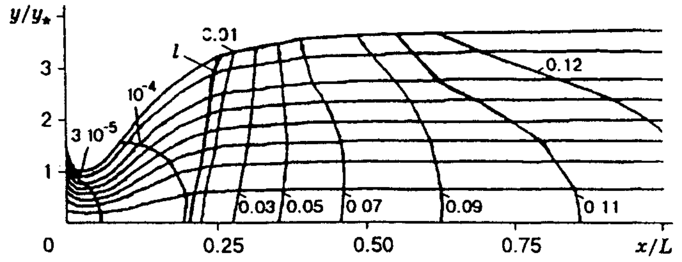

Fig. 1

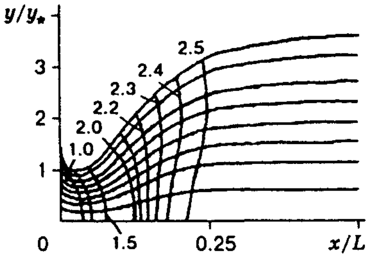

Fig. 2

where the first four parameters determine the parametric dependences of the flow field in the nozzle, and the last three determine the shape of the plane of the jump in concentration of O molecules. The concentration jump ΔO is assumed to be equal 0.1%.

In search for the optimum, we imposed the following restrictions on parameters (4.2): subject to $\alpha > 0$, $q \geqslant 0$, $0 < \beta \leqslant 1$, $0 < L < 20$, $0 < x'_* \leqslant 1$, $-50 \leqslant \gamma'_1/L \leqslant 50$, and $-50 \leqslant \gamma'_2/L \leqslant 50$.

Maximum values of the ozone concentration are sought by the following scheme. To decrease the computer time and determine the best initial point in the space of optimization parameters (4.2), the optimum is initially sought using the model of one-dimensional gas flow on the axis. In this case, the parameters over which optimization is performed are α, q, β, L, and x'_*. The optimization program synthesizes the methods of random and deterministic search. The random search is used in the initial stage of optimization. The method of configurations is used as a deterministic algorithm. Its principles are described in [9]. Search for an optimum for one-dimensional gas flow yields the following optimum parameters:

$$\alpha = 25.97, \quad q = 0.25, \quad \beta = 0.0588, \quad L = 11.7\,\text{cm}, \quad x'_* = 0.21, \tag{4.3}$$

which ensure a maximum value $\xi_3 = 0.10349\%$ of the molar fraction of ozone at the nozzle exit. Determination of the optimum set of parameters (4.3) required 232 references to the functional. The resulting values are taken as an initial point, and the optimum is further sought over parameters (4.2) under the assumption that the gas flow is two-dimensional. The integral of the concentration of ozone molecules at the nozzle exit is used as a functional:

$$F(A_i) = \xi'_3 = \frac{1}{\psi'_f} \int_0^{\psi'_f} \xi_3 d\psi'.$$

The fixed final value of the flow function $\psi'_f = 1.56 \cdot 10^{-2}$ $(0 \leqslant \psi' \leqslant \psi'_f)$ is considered. In this case, search for an optimum yields $\alpha = 34.87$, $q = 0.28$, $\beta = 0.0542$, $L = 13.47$ см, $x'_* = 0.202$, $\gamma'_1 = 22.14$, $\gamma'_2 = -174.2$, and $\xi'_3 = 0.1136\,\%$.

In this stage, it is necessary to refer to the functional $F(A_i)$ 48 times, which is far less than in determining parameters (4.3). This scheme of optimization procedure reduces considerably the total time of machine search, since the computer time necessary to calculate the flow field in the nozzle under the assumption of two-dimensional gas flow is approximately 1.5–2 orders of magnitude greater than the time required to determine a one-dimensional flow field.

Figure 1 shows the contour of a supersonic gas-dynamic nozzle obtained by solution of the optimization problem. The dimensionless length x/L is plotted on the abscissa, and the quantity y/y_* on the ordinate (y_* is the nozzle height in the minimum cross-section). The figure shows streamlines for various values of ψ = const and the lines of equal mole fractions of ozone. Curve l corresponds to the surface of jump in concentration $l(\psi)/L$ of atomic oxygen. The maximum slope of the contour of the supersonic part of the nozzle is attained at point $x/L \approx 0.1$ and is equal to 18°. It is seen that the part on which the nozzle expands rapidly must be followed by an extended plane-parallel part in which ozone is mainly formed. Figure 2 shows a similar pattern

TABLE 1

Variant number	$m_j^{(1)}$	$m_j^{(2)}$	O_3	$O_3^{(0)}$
0	1	1	1	1
1	0.5	2	0.47	0.45
2	0.5	0.5	0.89	0.82
3	2	2	1.12	1.05
4	2	0.5	1.54	1.52

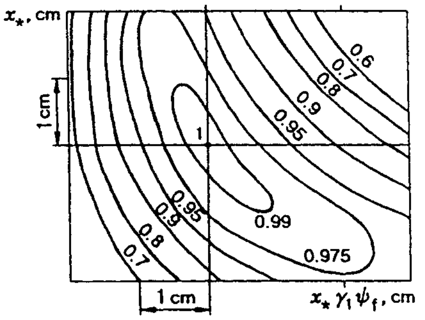

Fig. 3

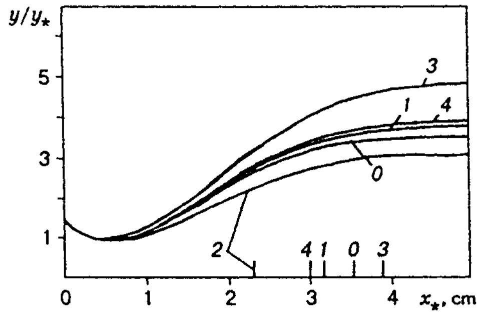

Fig. 4

of identical Mach numbers for the first half of the same optimum nozzle.

In the process of solving the problem of searching for an optimum, it is possible to determine, along with the optimum point, the topographic location of the levels of constant values of the functional under study (in our case, the mole fraction of ozone). For this, two different parameters A_1 and A_2 among those under optimization are chosen and varied. Values of the remaining parameters are fixed and set equal to the optimum values that correspond to optimization over the entire set of parameters. Next, lines of constant values of the tested functional are found in the plane (A_1, A_2). This provide not only a clear idea of the optimum found but also quantitative data on nonoptimum regimes near the optimum. Such data are of interest in conducting experiments and evaluating the "steepness" of change of the functional in the vicinity of the optimum.

Figure 3 shows the map of lines of equal ozone concentrations with respect to the parameters characterizing the location of the surface area of jump in concentration $l(\psi)$ of atomic oxygen in the nozzle. The parameters x'_* and γ'_1 which determine the jump plane are varied. The mole fraction of ozone ξ_3 at the optimum point is taken as unity. To simplify interpretation, the level curves in the figure are plotted for the quantities x_* and $x_*\gamma_1\psi_f$. It is evident that in the vicinity of the optimum the functional is gently sloping, but with distance from the optimum, the ozone concentration decreases greatly.

The current uncertainty in the rate constants of the processes considered can influence the shape of the optimum nozzle and the maximum ozone concentration. In this connection, a calculation (in a one-dimensional formulation) is first performed to clarify the effect of variation of the rate constants on the ozone concentration for the optimum set of parameters (4.3). For this, the rate constant K_j is varied as follows:

$$K_j = m_j K_j^0 \quad \text{and} \quad K_j = 1/m_j \cdot K_j^0, \tag{4.4}$$

where m_j is a constant and K_j^0 is the recommended constant from [5]. The ozone concentration (at the nozzle exit) is then calculated for this variation of the constant K_j. It turns out that the change in ozone concentration is primarily affected by ozone formation $O + O_2 + (M = O_2) \rightarrow O_3 + M$ (+33 and −34.4% at $m_j = 2$ and $1/m_j = 1/2$) and ozone dissociation $O + O_3 \rightarrow O_2 + O_2$ (−26.2 and +21.6% at $m_j = 2$ and $1/m_j = 1/2$). With this variation, the effect of the rate constants of other processes is less than 2%, and, hence, the two above-mentioned reactions are fundamental in the case at hand.

According to [5], the possible spread of the constants of these processes does not exceed 150–200%. Because of this, the optimization problem (in a one-dimensional formulation) can now be solved with maximum deviations of the constants K_j from the recommended K_j^0. The main results of the solution are presented in Table 1 and Fig. 4. In Table 1, $m_j^{(1)}$ corresponds to the factor m_j in (4.4) for the reaction $O + O_2 \rightarrow O_3$ ($M = O_2$), $m_j^{(2)}$ to the reaction $O + O_3 \rightarrow O_2 + O_2$, and O_3 to the optimal ozone concentration normalized to its value in (4.3), i.e., for $m_j \equiv 1$.

Figure 4 presents the optimum contours of supersonic nozzles obtained by solution of the optimization problem (with variation of the rate constants of the processes). Here, the length x is plotted on the abscissa and the dimensionless degree y/y_* of flow expansion on the ordinate. The curve numbers correspond to the variant numbers in the table and the symbol 0 designates the main contour for $m_j \equiv 1$. The vertical bars above the abscissa correspond to the jump coordinate x_* in a nozzle with the same number. The plane-parallel part of the nozzle is not presented in the figure. It is ~10 cm for all variations of the constants. The results presented in Table 1 and in Fig. 4 show that allowance for the uncertainty in the rate constants can influence significantly the results of solving the problem of a gas-dynamic ozonator. In this connection, the problem of refining these constants arises. On the other hand, the shape of the nozzle is not among the crucial factors that determine the numerical values of ozone concentration. This is evidenced by the data of Table 1 (the values for $O_3^{(0)}$) for ozone concentrations in the gas flow in the initial nozzle whose contour is designated by the symbol 0 in Fig. 4.

Thus, the program presented herein makes it possible to solve variational problems of gas dynamics with physicochemical transformations with the allowance for the two-dimensionality of the gas flow.

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