ANALYTIC METHOD FOR DETERMINING NONEQUILIBRIUM PARAMETERS OF AN AIR PLASMA IN A LAVAL NOZZLE

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The hierarchy of relaxation times of physicochemical processes occurring in an air plasma is examined. An engineering method for determining the nonequilibrium parameters of the plasma in a Laval nozzle is proposed.

Flows of relaxing gaseous media with sharp gradients and breakdown of equilibrium distribution of energy over the degrees of freedom of separate particles, changing the thermodynamic and thermophysical properties of the gas flow, which must be determined in order to perform laborious numerical calculations involving a large amount of computer time, are studied in a number of applied problems of gas dynamics [1, 2].

In addition to numerical methods, approximate analytical methods based on Bray's concept, which substantiates the model if instantaneous freezing of physicochemical processes in expanding flows of ideally dissociating gas, are also widely used [3, 4]. Under the conditions of flow of relaxing gases with sharp gradients, the instantaneous freezing model has been confirmed both numerically and experimentally to analyzing real gases [5, 6] and it was later extended to the case of vibrational relaxation [7] and chemically reacting media with complex composition [8].

According to Bray, the entire flow field can be divided into two sections: equilibrium and frozen, the boundary between which is determined by the section or, in the one-dimensional approximation, by the point of instantaneous freezing (PIF). In the case of a chemically reacting mixture, each component subjected to freezing has its own PIF. In a number of papers, to determine the PIF of the components, their equilibrium rate of change is equated either to a single determining recombination reaction rate [9] or to their algebraic sum [10]. In so doing, it is assumed that the exchange reactions occur practically at equilibrium.

These approaches are fundamentally incorrect, since the rate of transformation of the components is determined not by one or several slow three-particle recombination processes, but by exchange (chain) elementary chemical acts. And, the effect of recombination reactions becomes appreciable only at high densities of the medium.

In [11], to determine the PIF, the average molecular weight of the combustion products was chosen as the frozen parameter. This approach is justified if the main purpose of the calculation is to find the integral characteristics of the flow. A more correct approach from our point of view is to determine its PIF characteristics from the total enthalpy of the mixture [12], since the molecular weight, as will be shown in what follows, is insensitive to the values of the parameters at PIF.

In this paper, an engineering analytical method is proposed for determining the nonequilibrium parameters of a relaxing medium in a state of flow with a sharp gradient. In so doing, we examine the stationary one-dimensional flow of an ideal gas mixture through a Laval nozzle neglecting viscosity, heat conduction, and diffusion. The difference between this method and the methods mentioned above lies in the fact that the PIF of each component of the medium, in determining the nonequilibrium composition and vibrational energy, is found by comparing the characteristic time scale of the gasdynamic flow process to the corresponding effective values of its chemical and vibrational relaxation times [13, 14], including all the basic physicochemical processes in which the component examined participates. To determine the boundary separating equilibrium and frozen sections of the gas flow in the nozzle and the parameters of the flow, we used the idea of a point of instantaneous freezing of enthalpy (PIFE) of the gas as an energy factor, which reflects more completely the

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TABLE 1. Rate Constants of Physicochemical Processes in an Air Plasma [18-20]

No. of process	Plasma component	$\overline{K}_j$, cm³/mole·sec
1	M	$2{,}5\cdot10^{15\pm1}T^{-1/2}$ (a)
2	M	$1\cdot10^{18\pm1}T^{-1}$ (a)
3	M	$3{,}2\cdot10^{18\pm1}T^{-1}$ (a)
4		$1{,}8\cdot10^{8\pm0{,}3}T^{3/2}\exp(-3300/T)$
5		$1{,}5\cdot10^{13\pm0{,}3}$
6		$4{,}8\cdot10^{23}\,T^{-5/2}\exp(-43030/T)$
7		$2\cdot10^{19}\,T^{-1}$
8		$10^{-3}\,T\exp(-62{,}9\,T^{-1/3}+29{,}61)$
9		$10^{-3}\,T\exp(-62{,}9\,T^{-1/3}+31{,}13)$
10		$10^{-3}\,T\exp(-105{,}8\,T^{-1/3}+29{,}99)$
11	N_2, O_2, NO	$10^{-3}\,T\exp(-214{,}3\,T^{-1/3}+35{,}78)$
	N, O	$0{,}5\exp(-36{,}87\,T^{-1/3}+29{,}95)$ (б)
	Ar	$10^{-3}\,T\exp(-160{,}7\,T^{-1/3}+34{,}45)$
12	NO	$\exp(-36{,}87\,T^{-1/3}+29{,}95)$
	N_2, O_2	$10^{-3}\,T\exp(-62{,}9\,T^{-1/3}+29{,}32)$
	N, O	$2{,}2\cdot10^{13}$
	Ar	$\exp(-109\,T^{-1/3}+31{,}33)$
13	N_2, O_2, NO	$\exp(-166{,}3\,T^{-1/3}+37{,}76)$
	N, O	$5{,}0\exp(-36{,}87\,T^{-1/3}+29{,}95)$ (б)
	Ar	$10^{-3}\,T\exp(-160{,}7\,T^{-1/3}+34{,}45)$

Remark. a) Dimensionality of the contant is cm⁶/mole²·sec; b) constant was corrected taking account [19]; M is any component of the plasma.

process of internal physicochemical transformation in multicomponent gas mixtures. Since the concept of instantaneous freezing assumes isoentropicity of the equilibrium s and frozen f expansion processes of the relaxing gas [15], for the processes indicated (or sections of the flow), it is possible to determine the effective values of the adiabatic exponent and the molecular weight. This permits using to a good approximation, gasdynamic functions in the calculations [16] that express the instantaneous values of the flow parameters in terms of the reduced flow velocity λ.

As the relaxing medium, we shall examine an air plasma with a working temperature range 2000-6000°K and working pressure 0.01-100 bar. Under these conditions, the plasma is mainly a mixture of eight components: N_2, O_2, NO, N, O, Ar, NO^+, and e, between which the following reversible chemical reactions occur [17]:

$$O_2 + M + 5.1eV \underset{\overline{K_j}}{\overset{K_j}{\rightleftarrows}} O + O + M; \tag{1}$$

$$N_2 + M + 9.8eV \rightleftarrows N + N + M; \tag{2}$$

$$NO + M + 6.5eV \rightleftarrows N + O + M; \tag{3}$$

$$NO + O + 1.4eV \rightleftarrows O_2 + N; \tag{4}$$

$$N_2 + O + 3.3eV \rightleftarrows NO + N; \tag{5}$$

$$N_2 + O_2 + 1.9eV \rightleftarrows NO + NO; \tag{6}$$

$$N + O + 2.8eV \rightleftarrows NO^+ + e. \tag{7}$$

The exchange of vibrational energy between the components of the plasma in the single-quantum approximation can occur along the following channels [18]:

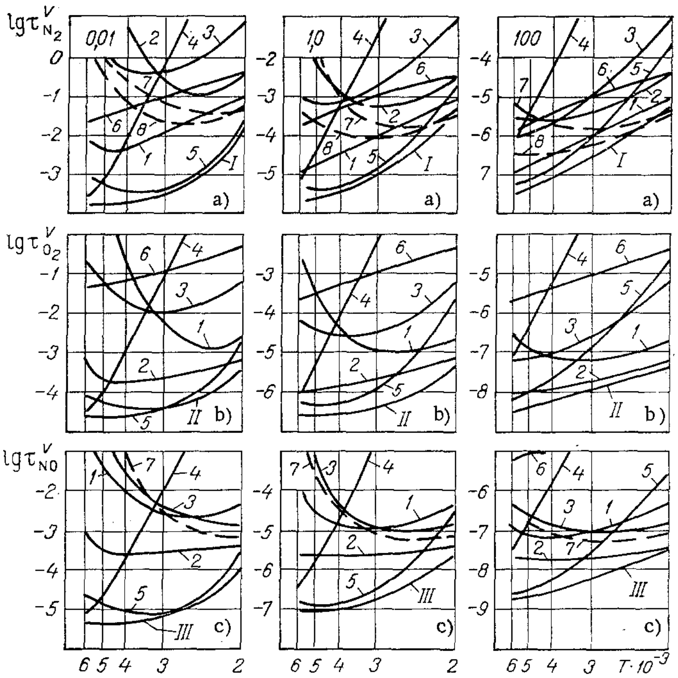


Fig. 1. Vibrational relaxation times of molecular components of an air plasma at pressures P = 0.01, 1.0, and 100 bar: a) 1$-N_2-N_2$; 2.7$-N_2-O_2$; 3.8$-N_2-$NO; 4$-N_2-$N; 5$-N_2-$O; 6$-N_2-$Ar; b) 1$-O_2-O_2$; 2$-O_2-N_2$; 3$-O_2-$NO; 4$-O_2-$N; 5$-O_2-$O; 6$-O_2-$Ar; c) 1$-$NO$-$NO; 2$-$NO$-N_2$; 3, 7 $-$ NO$-O_2$; 4$-$NO$-$N; 5$-$NO$-$O; 6$-$NO$-$Ar; the continuous and dashed lines show the VT and VV' relaxation times, respectively; I-III is the effective value of the relaxation time, sec. T,°K.

$$N_2(\vartheta = 0) + NO(\vartheta = 1) \rightleftarrows N_2(\vartheta = 1) + NO(\vartheta = 0); \tag{8}$$

$$NO(\vartheta = 0) + O_2(\vartheta = 1) \rightleftarrows NO(\vartheta = 1) + O_2(\vartheta = 0); \tag{9}$$

$$N_2(\vartheta = 0) + O_2(\vartheta = 1) \rightleftarrows N_2(\vartheta = 1) + O_2(\vartheta = 0); \tag{10}$$

$$N_2(\vartheta = 0) + M \rightleftarrows N_2(\vartheta = 1) + M; \tag{11}$$

$$NO(\vartheta = 0) + M \rightleftarrows NO(\vartheta = 1) + M; \tag{12}$$

$$O_2(\vartheta = 0) + M \rightleftarrows O_2(\vartheta = 1) + M. \tag{13}$$

Here M is any component of the plasma; K_j and $\bar{K}_j$ are the forward and backward rate constants of the j-th process, j = 1, 2, 3, ..., 13.

The interaction mechanism presented was analyzed assuming a quasiequilibrium flow of the physicochemical processes in the vibrational energy space of molecules, modeled as harmonic oscillators. In this case, the anharmonicity of the vibrational exchange was included by making appropriate corrections when examining the relaxation times and vibrational energy. The rate constants of the physicochemical processes used, from data in [18-20], are summarized in Table 1.

The position of the PIF of the plasma components can be found from the condition

$$ct_* = \tau_i, \tag{14}$$

where τ_i is the relaxation time of the i-th component in the physicochemical process; $t_* = \left|\frac{T}{dT/dt}\right|$ is the characteristic time scale of the gasdynamic process; c is a constant of order unity [8, 13].

Since the relaxation time by definition [21] is a function of equilibrium parameters, it can be used in the region $\tau \leq ct_*$, i.e., up to PIF, in the equilibrium region of variation of parameters and the composition of the medium. The characteristic time scale in the case of the adiabatic–isoentropic flow depends on the stagnation parameters and the geometrical dimensions of the nozzle. Thus, to determine the gas parameters at the PIF, it is not necessary to solve the equations of physicochemical kinetics. However, it is still necessary to solve numerically the equations of gasdynamics and a system of transcendental algebraic equations determining the equilibrium composition and relaxation time.

The method can be greatly simplified by finding the analytic dependences $\tau = f(P, T)$ and t_* on the gasdynamic parameters of the medium and the shape of the nozzle. Using (14), they permit finding the criterion for determining the parameters at the PIF, analogous to that presented in [7, 17]. Such a dependence for t_* is presented in [17] for a conical nozzle with a critical section with radius r_*. An analogous relation can also be obtained for a slit supersonic nozzle, formed by blades consisting of two half-cylinders with diameter d, triangular prisms with half-angle α and gap δ_* in the minimum transit section:

$$t_* = \left| \frac{\delta_* m_s^{3/2} (1 - \lambda^2) \bar{\mu}_s^{1/2} c_1}{4 n_s \lambda^4 (m_s - n_s \lambda^2)^{\Theta_s} \sqrt{\bar{k}_s R T_0}} \right|, \tag{15}$$

where $c_1 = 1/\sqrt{\{1 + \varphi[1 - \lambda^{-1}(m_s - n_s\lambda^2)^{-\Theta s}]\}^{-2} - 1}$ for $\lambda < 1$ and $\varphi = \delta_*/d$; $c_1 = 1/\tan\alpha$ for $\lambda > 1$.

As is evident from (15), the characteristic time scale is proportional to the height of the critical section of the nozzle and depends least on the molecular weight and stagnation temperature T_0 of the flow. Therefore, the use of the molecular weight to find the parameters of the medium at the PIF can lead to an additional methodological error.

Let us examine the relaxation times in the air plasma. Assuming that for the chosen range of parameters, the vibrational degrees of freedom of the molecular components have time to come into equilibrium with the translational degrees of freedom [17, 22], we shall analyze only the slowest processes: vibrational and chemical relaxation, as well as relaxation of the electron temperature.

The vibrational relaxation time in mixtures of molecular gases with flow in nozzles can greatly differ from the experimental values obtained in shock waves for "pure" gases [1]. Vibrational–vibrational (VV') energy exchange between different molecules can occur in mixtures of molecular gases together with VT and VV exchange of vibrational quanta. It is shown in [23, 24] that the vibrational relaxation time of nitrogen in a mixture with oxygen or a small admixture of nitrogen oxide is much smaller than for pure nitrogen. At high temperatures, dissociation is also important. In addition, the harmonic oscillator model, which is completely acceptable for examining processes occurring in shock waves, requires that anharmonicity be included in the case of flows in nozzles, where as a result of recombination processes the upper vibrational levels of molecules are greatly populated [1]. Here, VV exchange is excluded from the analysis, since it does not change the total vibrational energy of the molecules. As far as the relaxation times are concerned, for adiabatic collisions, occurring in an air plasma, the inequality $\tau_h^{VT} \gg \tau_h^{VV}$ is as a rule satisfied for the harmonic oscillator model [25]. The problem of the ratio of the VT and VV' relaxation times requires numerical analysis of the relaxation processes (8)-(13). The availability of experimental [18] and computational [19] data on relaxation constants permits using for this purpose the standard technique and analytic dependences for $\tau^{VT}{}_h$ and $\tau^{VV'}{}_h$, presented in [1, 25].

The computed temperature dependence of the vibrational relaxation times for N_2, O_2, and NO in an air plasma is presented in Fig. 1 for three values of the pressure (0.01, 1.0, and 100 bar). It is evident from the figure that at high temperatures and moderate pressures, the condition for slowed VV' exchange is satisfied for the effective relaxation times of N_2 and NO [25]:

$$\bar{\tau}^{VV} \ll \bar{\tau}^{VT} \ll \bar{\tau}^{VV'}, \tag{16}$$

related to the high degree of dissociation of molecular oxygen and nitrogen oxide. In this case, atomic oxygen and nitrogen make the main contribution to VT exchange of vibrational energy at high temperatures.

The dependence of the effective relaxation time of vibrational VT exchange of the basic molecular components in an air plasma on the temperature and pressure can be represented in terms of the following approximating polynomials:

$$\begin{aligned}
\lg \bar{\tau}^{VT}_{(N_2)} &= 1.56\,(Z^{-1} + 4.04 \lg Z - 4.33) - 0.26 \lg P\,(Z^{-1} + 7.28 \lg Z + 3.6);\\
\lg \bar{\tau}^{VT}_{(O_2)} &= 0.82\,(Z^{-1} + 3.87 \lg Z - 8.75) - 0.18 \lg P\,(Z^{-1} + 6.39 \lg Z + 4.89);\\
\lg \bar{\tau}^{VT}_{(NO)} &= 0.97\,(Z^{-1} + 4.13 \lg Z - 7.9) - 0.07 \lg P\,(Z^{-1} + 4.73 \lg Z + 12.52).
\end{aligned} \tag{17}$$

(17)

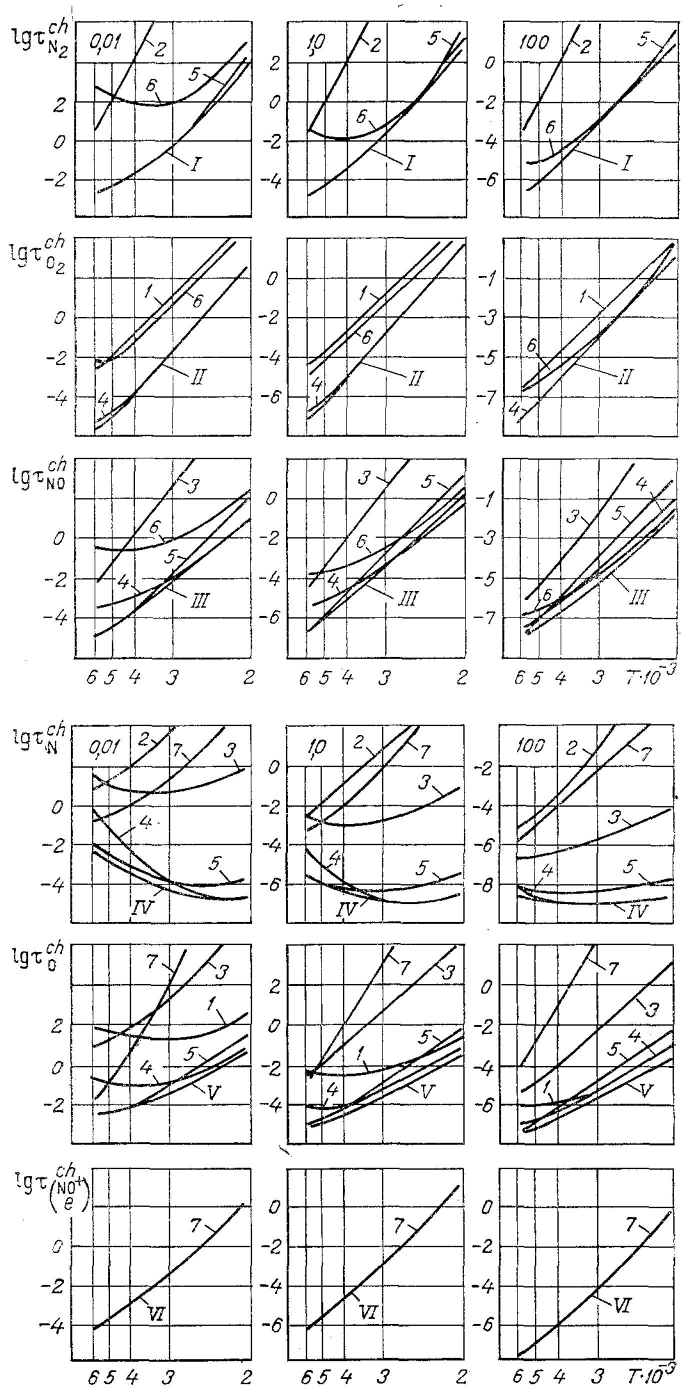


Fig. 2. Chemical relaxation times for components in an air plasma at pressures P = 0.01, 1.0, and 100 bar: 1-7) number of chemical reactions; I-VI) effective values of the relaxation time, sec.

Here and in what follows, Z = T·10^{-4},°K; P, bar; $\bar{\tau}^{VT}_{(i)}$, sec. The error in determining $\bar{\tau}^{VT}$ from (17) does not exceed 20% in the indicated range of temperatures and pressures.

The effect of anharmonicity on the value of the vibrational relaxation time for a VT process, when the condition $T_{ki} < \Theta_{Vi}/\ln \gamma_i'$ is satisfied, can be included by the correction [1]

$$n_i^a = \frac{\tau_a^V}{\tau_h^V} \simeq \left[\frac{1-\gamma_i' \exp(-\Theta_{Vi}/T_{\text{к}i})}{1-\exp(-\Theta_{Vi}/T_{\text{к}i})}\right]^2, \qquad (18)$$

where $\gamma_i' \simeq \exp(1.87\Theta_{Vi}^{2/3} T_{ki}^{-1/3} x_{ei})$. Since before the corresponding PIF, the vibrational temperature of the molecules equals the translational temperature, and after the PIF T_{ki} = const, the working relations for finding n_i^a can be specified and represented as a function of the translational temperature:

$$n_{N_2}^a = 0.54Z^{-0,49}\exp(-0.056/Z);\ n_{O_2}^a = 0.\ 36Z^{-0,77}\exp(-0.083/Z); \tag{19}$$
$$n_{NO}^a = 0,41Z^{-0,7}\exp(-0.077/Z).$$

We shall now analyze the chemical relaxation time. The technique and analytic dependences for finding it were obtained in [21, 26]. For an air plasma, the working relations for $\tau_i{}^{ch}$ are presented in [14].

In this paper, in calculating the chemical relaxation times, whose temperature dependences are presented in Fig. 2 for three values of the pressure (0.01, 1.0, and 100 bar), averaged values of the recombination rate constants $\bar{K}_j$ were used [20]. The values of the forward rate constants for the reactions K_j were found using the equilibrium constants. Under conditions when $\bar{\tau}_i \leq t_*$, this approach does not give rise to any doubts, since in this region each component is located near a state of thermodynamic equilibrium.

It is evident from the figure that the three-particle recombination reactions have an appreciable effect on the value of the effective relaxation time only at high plasma pressures. For medium and low pressures, Ya. B. Zel'dovich's chain mechanism is determined [21], which confirms the validity of our remarks concerning the techniques examined above [9-11].

The temperature and pressure dependence of the effective chemical relaxation time of the components in an air plasma can be represented in terms of the following polynomials:

$$\begin{gathered}
\lg \bar{\tau}_{(N)}^{ch} = 1{,}42(Z^{-1} + 9\lg Z - 3.5) - 0.5\lg P(-Z^{-1} + 23{,}33\lg Z + 39.92);\\
\lg \bar{\tau}_{(O)}^{ch} = 1{,}75(Z^{-1} + 2.5\lg Z - 4) - 0.6\lg P(Z^{-1} + 7.5\lg Z + 2.15);\\
\lg \bar{\tau}_{(NO^+)}^{ch} + 3.34(Z^{-1} + 2.3\lg Z - 2.99) - 0.25\lg P(Z^{-1} + 9.1\lg Z + 3.54);\\
\lg \bar{\tau}_{(N_2)}^{ch} = 3.82(Z^{-1} + 2.8\lg Z - 2{,}31) - 0.37\lg P(Z^{-1} + 8{,}38\lg Z + 2.92);\\
\lg \bar{\tau}_{(O_2)}^{ch} = 3{,}27(Z^{-1} + 1.32\lg Z - 3.55) - 0.42\lg P(Z^{-1} + 6.57\lg Z + 1.24);\\
\lg \bar{\tau}_{(NO)}^{ch} = 2{,}22(Z^{-1} + 0{,}69\lg Z - 4{,}55) - 0.5\lg P(Z^{-1} + 6.82\lg Z + 1.33).
\end{gathered} \tag{20}$$

The error in determining $\bar{\tau}_i{}^{ch}$ from (20) does not exceed 50% in the temperature and pressure ranges examined.

The points of instantaneous freezing of each of the plasma components have their own instantaneous values of the thermodynamic flow temperature $T = f(\lambda)$ and pressure $P = f(\lambda)$, which are the starting data for finding the equilibrium composition of the flow at PIF. The frozen particles of the plasma practically do not change their molar mass concentration after PIF right up to the nozzle exit. The influence of components subjected to previous freezing on the position of the PIF of the remaining components is negligibly small, as demonstrated by the numerical calculations. The following material balance relation can be taken as the criterion for accuracy in determining the nonequilibrium composition in the frozen flow of an air plasma:

$$\frac{\gamma_{(N)} + \gamma_{(NO)} + 2\gamma_{(N_2)}}{\gamma_{(O)} + \gamma_{(NO)} + 2\gamma_{(O_2)}} = \text{const.} \tag{21}$$

In the range of temperatures and pressures indicated, breakdown of ionization equilibrium with efflux of plasma from the nozzle occurs not only due to freezing of the ion and electron density, but also due to the deviation of the electron temperature T_e from the translational temperature of the heavy particles.

The effective relaxation time of the electron temperature [21] is found from the equation

$$\bar{\tau}_e^{-1} = \tau_{ei}^{-1} + \tau_{ea}^{-1}, \tag{22}$$

where the relaxation time for exchange of energy between electrons and ions τ_{ei} and between electrons and neutral particles τ_{ea} in an air plasma can be determined from the following relations:

$$\tau_{ei} = 1.24 \cdot 10^{-17}\frac{T_e^{3/2}}{\rho\gamma_{(NO^+)}\ln\Lambda};$$

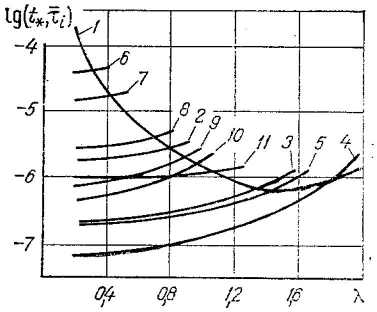


Fig. 3. Characteristic time scale and relaxation times of physicochemical processes in a Laval nozzle as a function of the reduced velocity: 1) t_*, $\bar{\tau}_i^V$; 2) N_2; 3) O_2; 4) NO; 5) $\bar{\tau}_e$; $\bar{\tau}_i$ch; 6) N_2; 7) 0; 8) NO^+; 9) NO; 10) O_2; 11) N, sec.

$$\tau_{ea} = 2\cdot 10^{-29} \frac{T_e^{1/2}}{P\sum\limits_i \gamma_a Q_a}; \; \Lambda = 2.53\cdot 10^{-7} \frac{T_e^{3/2}}{\sqrt{\rho\gamma_{(NO^+)}}}; \tag{23}$$

here P is in bar; ρ, kg/m^3; γ_i, kmole/kg; Q_a, m^2; $\bar{\tau}_e$, sec.

To illustrate the computational technique, we shall examine a specific example of efflux of an air plasma from a flat Laval nozzle. The stagnation parameters of the plasma are: T_0 = 5000°K; P_0 = 1 bar; a_0 = 1447 m/sec; k_0 = 1.22; μ_0 = 23.9. The geometric dimensions of the nozzle are $d = 2\cdot 10^{-3}$ m; α = 15°; $\delta_* = 2\cdot 10^{-4}$ m; and H = const.

The characteristic time scale (curve 1), the vibrational and chemical relaxation times, and the relaxation time of the electron temperature are presented in Fig. 3 as a function of the reduced velocity λ with adiabatic–isoentropic expansion of the air plasma in the nozzle. The points of intersection of the curve 1 with the remaining curves correspond to the PIF of vibrational energy, electron temperature, and plasma components.

The position of the PIF of the enthalpy of the flow is found from the condition $I_s(T) = I_f(T)$, expressing the equality of the enthalpy of the equilibrium $I_s(T)$ and frozen $I_f(T)$ regimes of the gas flow in the transitional region. In this case

$$I_s = I_0 - a_0^2\Theta_s(1 - T/T_0); \tag{24}$$

$$I_f = \sum_i^M (I_i + \Delta E_{Vi})\gamma_{if} + \sum_i^A I_i\gamma_{if}; \tag{25}$$

$$\Delta E_{Vi} = E_{Vi}^f - (E_{Vi}^h + \Delta E_{Vi}^a); \; E_{Vi}^h = \frac{R\Theta_{Vi}}{\exp(\Theta_{Vi}/T) - 1}. \tag{26}$$

Here E^f_{Vi} (J/mole) is the frozen value of the vibrational energy of the i-th molecular component (before PIF $E^f_{Vi} = E^h_{Vi} + \Delta E^a_{Vi}$); ΔE^a_{Vi} is the correction to the vibrational energy that includes the anharmonicity of the vibrations and their interaction with molecular rotation [27].

The working relations for finding ΔE_{Vi} can be specified and represented as functions of the temperatures T_V and T:

$$\begin{aligned} \Delta E_{V(N_2)} &= 2315\left(\frac{Z_V + 12.21}{1.4^{1/Z_V} - 1} - \frac{Z + 12.21}{1.4^{1/Z} - 1}\right); \\ \Delta E_{V(O_2)} &= 2870\left(\frac{Z_V + 6.59}{1.25^{1/Z_V} - 1} - \frac{Z + 6.59}{1.25^{1/Z} - 1}\right); \\ \Delta E_{V(NO)} &= 2807\left(\frac{Z_V + 8.12}{1.31^{1/Z_V} - 1} - \frac{Z + 8.12}{1.31^{1/Z} - 1}\right). \end{aligned} \tag{27}$$

The function $I_f(T)$ is almost linear, so that relation (25) can be represented in the form

$$I_f = c_{pf}T + A, \tag{28}$$

where $c_{pf} = \Delta I_f/\Delta T$; $A = \sum\limits_i^M (\Delta_f H_i^0 + \Delta E_{Vi}|_{T=0})\gamma_{if} + \sum\limits_i^A \Delta_f H_i^0\gamma_{if}$. Here $\Delta_f H_i^0$ is the formation enthalpy of the i-th component in the standard state at T = 0°K.

TABLE 2. Comparative Characteristics of an Air Plasma at the Nozzle Cut Off in Equilibrium (s, first row) and Real (s-f, second row) Efflux Processes (T, K; P, bar; W, m/sec)

Composition, kmole/kg						
$\gamma(N_2)\cdot 10^2$	$\gamma(O_2)\cdot 10^4$	$\gamma(NO)\cdot 10^4$	$\gamma(N)\cdot 10^7$	$\gamma(O)\cdot 10^4$	$\gamma(NO^+)\cdot 10^{10}$	$\gamma(Ar)\cdot 10^4$
2,67 2,61	68,28 1,79	4,26 8,71	0,033 3810	3,79 134	0,0456 11605	3,35 3,35
T_{ne}	$P_{ne}\cdot 10^2$	W_{ne}	$T_V(N_2)$	$T_V(O_2)$	$T_V(NO)$	T_e
2190 1092	1,04 0,58	3266 3076	2190 4704	2190 3994	2190 3419	2190 4083

The plasma parameters at the PIFE and its location are found from the relation

$$T^* = \left(\frac{I_0 - a_0^2\Theta_s - A}{c_{pf} - a_0^2\Theta_s T_0^{-1}}\right); \quad \rho^* = \rho_0\left(\frac{T^*}{T_0}\right)^{\Theta_s};$$

$$P^* = P_0\left(\frac{T^*}{T_0}\right)^{\theta_s}; \quad W^* = a_0\sqrt{2\Theta_s(1 - T^*/T_0)};$$

$$\lambda^* = \sqrt{\frac{m_s}{n_s}(1 - T^*/T_0)}; \quad F^* = \frac{\delta_* H}{\lambda^*(m_s - n_s\lambda^{*2})^{\Theta_s}}, \tag{29}$$

while at the nozzle exit, it is found from the solution of the system of equations

$$W_{ne} = \sqrt{2(I_0 - c_{pf}T_{ne} - A)}; \quad \overline{\mu}_f = 1/\sum_i \gamma_{if};$$

$$\rho_{ne}W_{ne}F_{ne} = \rho^* W^* F^*; \quad \rho_{ne} = \frac{P_{ne}\mu_f}{RT_{ne}}; \tag{30}$$

$$\frac{P_{ne}}{P^*} = \left(\frac{T_{ne}}{T^*}\right)^{\theta f}; \quad k_f = \frac{c_{pf}}{c_{pf} - R/\mu_f}.$$

The system (30) can be reduced to an equation with a single unknown T_C:

$$W^*\frac{F^*}{F_{ne}}\left(\frac{T^*}{T_{ne}}\right)^{\Theta f} = \sqrt{2(I_0 - c_{pf}T_{ne} - A)}, \tag{31}$$

after determining which, there is no difficulty in finding the values of the remaining parameters.

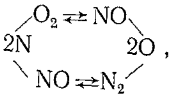
The computed equilibrium values of the parameters of an air plasma in the exit section of the nozzle (s-f), as well as the value of plasma parameters with equilibrium adiabatic–isoentropic efflux (s) are presented in Table 2 for given initial conditions (T_0, P_0). Analysis of the results of the calculation shows that nonequilibrium processes have a considerable effect on the temperature and pressure and quite insignificant effect on the velocity and density, and therefore, on the velocity head and stagnation pressure. The error in determining the nonequilibrium composition, found from (21), is about 2%.

Dissipation of energy and heat exchange with the external environment can be included by comparatively simple experimental measurements of heat transfer to the nozzle wall (Q^e_{cond}) and the static pressure at its exit (P^e_{ne}). The effect of heat exchange on the degree of cooling of the gas and, therefore, on the position of the PIF of its components in the initial (accelerating) section of the nozzle is comparatively small and can be included, when necessary, with a small correction in the relation for t_*. In this case, the velocity of the frozen flow and its temperature at the nozzle exit at fixed stagnation enthalpy of the flow at the inlet I_0 and gas flow rate G are determined by relations following from the equations of energy, state, and continuity:

$$T_{ne} = W_{ne}\frac{P^e_{ne}\overline{\mu}_f F_{ne}}{RG}; \tag{32}$$

$$0.5W_{ne}^2 + \frac{c_{pf}P^e_{ne}\overline{\mu}_f F_{ne}}{RG}W_{ne} - \left(I_0 - A - \frac{Q^e_{cool}}{G}\right) = 0.$$

Analysis of the hierarchy of effective values of the relaxation times for physicochemical processes in an air plasma, as the plasma expands in small nozzles, whose transverse cross-sectional area varies according to a power law $F \sim X^n$, shows that such flows can be successfully calculated using equilibrium physicochemical kinetics. The following inequalities are satisfied for its basic macrosystems, including molecular and atomic particles, in the indicated range of temperatures and moderate pressures: $\bar{\tau}^{ch} \gg \bar{\tau}^{V} \gg \tau^{R} > \bar{\tau}^{T}$. For this reason, chemical relaxation, occurring primarily through exchange reactions according to the scheme



occurs practically under conditions of equilibrium flow of intermolecular vibrational exchange (see Fig. 3). The use of multilevel physical kinetics in the analysis of analogous systems will not fundamentally change the results obtained, since it, to a large extent, will lower the vibrational relaxation time of the molecular components [25].

The interrelation of the relaxation processes and chemical transformations in gases has now been studied well only in the case of thermal dissociation of pure molecular gases [25]. For exchange chemical reactions, which are determining in the chemical kinetics of an air plasma, there are practically no such data. The dependences presented in [20] (see Table 1) permit estimating in a first, quite rough approximation the effect of the nonequilibrium nature of processes on the values of the rate constants of exchange reactions.

The proposed method differs from the simple determination of nonequilibrium values of parameters. It can be used in cases when aside from the integral characteristics of the efflux process, it is necessary to know the frozen composition, temperature of internal degrees of freedom of components, as well as the effect of the geometric dimensions of the nozzle on the degree of deviation of the composition and parameters of the gas flow from its corresponding equilibrium values.

NOTATION

T and T_V, temperatures of the translational and vibrational degrees of freedom of the gas; Θ_{Vi}, characteristic vibrational temperature of the molecules; P, pressure; ρ, density; μ, molecular weight; $\bar{\mu}$, effective molecular weight; k, adiabatic exponent; $\bar{k}$, effective adiabatic exponent; W, velocity of the flow; a, velocity of sound; I_i, specific enthalpy of the i-th component; c_p, heat capacity of the gas; R, universal gas constant; γ_i, γ_a, molar-mass concentration of any i-th component of the gas and its neutral particle; Q_a, effective cross section of elastic electron–neutrals collisions; $\ln\Lambda$, Coulomb logarithm of electron–ion interaction; x_e, spectroscopic constant; $E^h{}_{Vi}$, specific vibrational energy of molecules in a system of harmonic oscillators; $\tau_h{}^V$, $\tau_a{}^V$, vibrational relaxation times for systems of harmonic and anharmonic oscillators; τ^R, τ^T, relaxation times for the rotational and translational degrees of freedom; $\bar{\tau}_i$, effective relaxation time of the i-th component in the physicochemical process; F, cross section of the nozzle; $\lambda = W/a_*$, reduced velocity; $m_s = 0.5(\bar{k}_s + 1)$; $n_s = 0.5(\bar{k}_s - 1)$; $\Theta_s = 1/(\bar{k}_s - 1)$; $\theta_s = \Theta_s \bar{k}_s$; $\bar{k}_s = (k_* - k_0)/\ln(k_* - k_0)$; $\bar{\mu}_s = (\mu_* - \mu_0)/\ln(\mu_* - \mu_0)$; $\Theta_f = 1/(\bar{k}_f - 1)$; $\theta_f = \Theta_f \bar{k}_f$; and $\sum_i^A$, $\sum_i^M$, indicates summation over atomic and molecular components. The indices are as follows: 0, stagnation parameters; s, equilibrium values; f, a frozen value; *, at PIF enthalpy; *, at the critical section of the nozzle.

LITERATURE CITED

1. S. A. Losev, Gas Dynamic Lasers [in Russian], Nauka, Moscow (1977).
2. V. M. Khailov, Chemical Relaxation in Jet Engine Nozzles [in Russian], Mashinostroenie, Moscow (1975).
3. K. N. C. Brey, "Atomic recombination in a hypersonic wind-tunnel nozzle," Fluid Mech., VII, 6, No. 1, 1-32 (1959).
4. K. N. C. Bray, "Chemical reactions in supersonic nozzle flows," Ninth Symposium (Int.) on Combustion, Academic Press, New York (1963), pp. 770-782.
5. Lordy and Mates, "Nonequilibrium effects accompanying expansion of air with high stagnation enthalpy," Raket. Tekh. Kosmon., 3, No. 10, 249-251 (1965).

6. E. A. Lezberg, C. M. Rose, and R. Friedman, "Experimental measurements of hydroxyl radical concentration in a hydrogen–air nozzle and comparison with kinetic calculations," AIAA Paper, 65-579, 22-25 (1965).
7. Kazuhiko Horioka, Koichi Kasuya, Keishiro Niu, and Tishimitsu Murasaki, "Comparisons between numerical and approximate solutions for vibrational nonequilibrium nozzle flows of CO_2–N_2 mixtures," Jpn. J. Appl. Phys., 17, No. 7, 1927-1928 (1978).
8. Wild, "Investigation of adiabatic flow including nonequilibrium chemical reactions for fuels containing C, H, O, and N atoms," Raket. Tekh. Kosmon., 3, No. 10, 72-76 (1965).
9. D. J. Simkin and R. R. Koppang, "Recombination losses in rocket nozzles with storable propellants," AIAA J., 1, No. 9, 2151-2153 (1963).
10. R. Kushida, "Nonequilibrium chemical recombination effects in exhaust nozzle flow: An approximate method," AIAA Progress in Astronautics and Rocketry: Liquid Rockets and Propellants, Vol. 2, Academic Press, New York (1960), pp. 385-409.
11. L. C. Fransiscus and E. A. Lezberg, "Effects of exhaust nozzle recombination on hypersonic ramjet performance: II. Analytical investigation," AIAA J., 1, No. 9, 2077-2083 (1963).
12. V. A. Reisig, S. A. Stadnik, and G. M. Shchegolev, "Investigation of chemical and ionization nonequilibrium state in supersonic flows of combustion products," Proceedings of All-Union Scientific–Technical Conference on Thermodynamics, Leningrad (1969), pp. 100-103.
13. F. I. Zakharov and V. A. Reisig, "Calculation of parameters of an air plasma with adiabatic expansion in a micronozzle lattice," in: Direct Energy Conversion [in Russian], Naukova Dumka, Kiev (1980), pp. 72-78.
14. F. I. Zakharov and V. A. Reisig, "Relaxation time of physicochemical processes in an air plasma," in: Conversion of MHD Energy by a Thermoelectric Method [in Russian], Naukova Dumka, Kiev (1981), pp. 110-120.
15. A. O. Eschenroeder, "Entropy changes in nonequilibrium flows," Phys. Fluids, X, 6, No. 10, 1408-1419 (1963).
16. Yu. D. Irov, É. V. Keil', B. N. Maslov, et al., Gas Dynamic Functions [in Russian], Mashinostroenie, Moscow (1965).
17. V. P. Agafonov, V. K. Vertushkin, A. A. Gladkov, and O. Yu. Polyanskii, Nonequilibrium Physicochemical Processes in Aerodynamics [in Russian], Mashinostroenie, Moscow (1972).
18. A. P. Zuev, B. K. Tkachenko, and V. P. Vakatov, "Experimental determination of nonequilibrium effects accompanying thermal decomposition of N_2O," Proceedings of the Sixth All-Union Symposium on Combustion and Explosion (Alma-Ata). Chemical Physics of Combustion and Explosion Processes. Kinetics of Chemical Reactions, Chernogolovka (1980), pp. 10-13.
19. E. A. Andreev and E. A. Nikitin, "Transfer of vibrational and electronic energy in atomic–molecular collisions," in: Chemistry of Plasma [in Russian], B. M. Smirnov (ed.), No. 3, Atomizdat, Moscow (1976), pp. 28-94.
20. J. Martin, Entrance into the Atmosphere. Introduction to Theory and Practice [Russian translation], Mir, Moscow (1969).
21. Ya. B. Zel'dovich and Yu. P. Raizer, Physics of Shock Waves and High Temperature Hydrodynamic Phenomena, Academic Press.
22. E. V. Stupachenko, S. A. Losev, and A. I. Osipov, Relaxation Processes in Shock Waves [in Russian], Nauka, Moscow (1965).
23. White and Millikan, "Vibrational relaxation in air," Raket. Tekh. Kosmon., 2, No. 10, 213-215 (1964).
24. R. L. Taylor, M. Camac, and R. M. Feinberg, "Measurements of vibration–vibration coupling in gas mixtures," Eleventh Symposium (Int.) on Combusion, Academic Press, New York (1967), pp. 49-66.
25. B. F. Gordiets, A. I. Osipov, and L. A. Shelepin, Kinetic Processes in Gases and Molecular Lasers [in Russian], Nauka, Moscow (1980).
26. V. A. Reisig and V. P. Kubaichuk, "Calculation of parameters of low temperature plasma including relaxation time of bi- and trimolecular chemical processes, " in: Thermophysical Problems of Direct Energy Conversion [in Russian], Naukova Dumka, Kiev (1979), pp. 44-47.
27. Tsyan' Syué-cen', Physical Mechanics [Russian translation], Mir, Moscow (1965).