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DETERMINATION OF THE MECHANISM OF PHYSICOCHEMICAL PROCESSES IN HIGH-TEMPERATURE AIR

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At high temperatures (tens of thousands of degrees), the kinetics of physicochemical processes in air is characterized by the fact that vibrational relaxation goes simultaneously with dissociation of N_2 and O_2 molecules. Such conditions correspond, in particular, to strong shock waves in air which arise in the nose part of an aircraft entering dense atmospheric layers.

To determine correctly the kinetic and gas-dynamic characteristics, the equations of gas dynamics must be integrated together with the equations of chemical kinetics and vibrational relaxation, with allowance for their mutual influence.

This work presents data on the rate constants of the kinetics of physicochemical processes in air. The data are approximated up to high temperatures (up to 100,000 K). By using a two-temperature dissociation model for N_2 and O_2 molecules, a calculation is conducted behind a shock wave propagating in the atmosphere at an altitude of 70 km.

The problem of simplifying a complex system describing the kinetics of physicochemical processes in a gas is considered. An algorithm is suggested that makes it possible to single out the leading processes in the system that takes into account a large number of physicochemical stages. The algorithm is based on building a hierarchy of stages of a complex physicochemical process as a result of comparing the rates of individual processes. The algorithm is demonstrated to be operational for determining the mechanism of the leading processes in air at high temperatures (several thousands degrees). It is shown that the mechanism of physicochemical processes in a gas can be significantly simplified.

1. Kinetic Equations. Let us assume that a gas consists of n components participating in m reactions of the type

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

Here, K_j is the constant of the direct reaction rate; ν_{ij}^{+} and ν_{ij}^{-} are stoichiometric coefficients; Y_i's are the initial materials and reaction products. The reverse reaction with rate constant K_{-j} is written similarly. If one uses mole–mass concentrations $c_i = N_i/(N_{\rm A}\rho)$ to determine the concentrations of the given material, the phenomenological equations of chemical kinetics have the form

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

where $i = 1, 2, \ldots, n$; t is the time; N_i is the concentration of particles per cm^3; $N_{\rm A}$ is the Avogadro number; ρ is the density of the gas mixture.

Relaxation equations for vibrational energy will be used under the following assumptions:

— each type of vibrations is modeled by a harmonic oscillator;

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— within each mode the energy exchange proceeds much faster 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 conserved.

The system of relaxation equations for vibrational energy is written with respect to $e_i = [\exp(\Theta_i/T_{Vi}) - 1]^{-1}$, which is the average number of vibrational quanta of the ith type per one molecule (Θ_i is the characteristic vibrational temperature and T_{Vi} is the vibrational temperature) [1]:

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

Here the first term takes into account the vibrational–translational VT-exchange; the second term takes into account the intermode VV'-exchange; and the third, the change in vibrational energy due to chemical reactions involving vibrationally induced molecules (the CV-process). The terms Q^i_{VT} and $Q^i_{VV'}$ can be represented in the form

$$Q^i_{VT} = \frac{e^0_i - e_i}{\tau_i}, \qquad \tau_i = \left[\sum_{j=1}^{n} \frac{c_j}{\tau_{ij} \sum\limits_k c_k}\right]^{-1}, \qquad Q^i_{VV'} = k_{im}[e_m(e_i + 1)\exp(\Theta_m/T - \Theta_i/T) - e_i(e_m + 1)],$$

where e^0_i is the equilibrium value of the vibrational energy e_i at $T_{Vi} = T$; τ_{ij} is the time of vibrational relaxation of the i mode after collision with molecules of type j; k_{im} is the rate constant of the VV'-exchange between the i and m molecules (modes); Θ_i and Θ_m are the corresponding characteristic vibrational temperatures; the expression $Q^i_{VV'}$ is written for the one-quantum exchange between molecules. In the case of a multiquantum exchange, $Q^i_{VV'}$ takes a somewhat more complicated form [2].

The term Q^i_{CV} [1] takes into account the change in the vibrational energy e_i of the ith type of vibrations in the jth molecule, resulting from chemical reactions:

$$Q^i_{CV} = \frac{1}{\rho c_j} \sum_{k=1}^{m} \left(\nu^-_{jk} - \nu^+_{jk}\right)(e^*_{ik} - e_i) S_k \,. \tag{1.1}$$

Here, S_k is the rate of the kth chemical reaction; e^*_{ik} is the mean value of the vibrational energy that is lost (or gained) by an i-type mode in each act of a chemical reaction of type k.

For the moving gas, the kinetic equations must be integrated together with the equations of gas dynamics.

2. Rate Constants of Processes in Air. The basic processes in high-temperature air are

— the dissociation and recombination of the N_2, O_2, and NO molecules

$$N_2 + M \leftrightarrow 2N + M, \qquad O_2 + M \leftrightarrow 2O + M, \qquad NO + M \leftrightarrow N + O + M \qquad (M \text{ — is any particle});$$

— the exchange reactions

$$N_2 + O \leftrightarrow NO + N, \qquad O_2 + N \leftrightarrow NO + O, \qquad N_2 + O_2 \leftrightarrow NO + NO;$$

— the associative ionization reactions

$$N + O \leftrightarrow NO^+ + e, \qquad O + O \leftrightarrow O_2^+ + e, \qquad N + N \leftrightarrow N_2^+ + e;$$

— the processes of ionization by an electron shock

$$O_2 + e \leftrightarrow O_2^+ + 2e, \quad N_2 + e \leftrightarrow N_2^+ + 2e, \quad NO + e \leftrightarrow NO^+ + 2e, \quad O + e \leftrightarrow O^+ + 2e, \quad N + e \leftrightarrow N^+ + 2e;$$

— the charge-exchange reactions and ion–molecular reactions

$$O + N^+ \leftrightarrow O^+ + N, \quad NO^+ + NO \leftrightarrow N_2 + O_2^+, \quad O_2^+ + N_2 \leftrightarrow O_2 + N_2^+, \quad NO^+ + NO \leftrightarrow O_2 + N_2^+,$$

$$NO^+ + N_2 \leftrightarrow NO + N_2^+, \quad N_2^+ + O \leftrightarrow NO + N^+, \quad O_2^+ + N \leftrightarrow O_2 + N^+, \quad NO^+ + N \leftrightarrow N_2 + O^+,$$

$$O_2^+ + O \leftrightarrow O_2 + O^+, \quad NO^+ + N \leftrightarrow N_2^+ + O, \quad O^+ + N_2 \leftrightarrow O + N_2^+, \quad NO^+ + O \leftrightarrow N^+ + O_2,$$

$$NO^+ + O \leftrightarrow NO + O^+, \quad NO^+ + O \leftrightarrow O_2^+ + N, \quad NO^+ + O_2 \leftrightarrow NO + O_2^+, \quad N_2 + N^+ \leftrightarrow N_2^+ + N;$$

— the emission due to collision with an electron

$$O^+ + e \to O + h\nu, \qquad N^+ + e \to N + h\nu,$$

— the emission of excited molecules;

— the VT-exchange of the N_2 and O_2 molecules;

— the VV'-exchange between the following pairs of molecules: N_2–O_2, O_2–NO, and N_2–NO, and also the CV-process, which we took into account for the case of dissociation and recombination of the N_2 and O_2 molecules and for the exchange reaction $N_2 + O \leftrightarrow NO + N$ (see the discussion in [1]).

A full list of processes and rate constants taken into account is given in [1]. In addition to [1], we present here the results of approximating the times of vibrational relaxation of the N_2 and O_2 molecules in the temperature range from 200 to 100,000 K (Table 1). To approximate the chemical reaction rate constants, we used the Arrhenius dependence for both direct and reverse reactions (Table 2). Here we also present the single-temperature rate constants for the dissociation and recombination of N_2, O_2, and NO molecules that are recommended by the AVOGADRO system.

In calculating the reaction rate constant K_j for the reaction involving electrons, one must substitute the electron temperature T_e as an argument. It was assumed in the calculations that $T_e = T_V$ (to be more precise, $T_e = \xi_1 T_{V1} + \xi_2 T_{V2}$, where ξ_i and T_{Vi} are the molar fractions and vibrational temperatures of the O_2 and N_2 molecules) because of the great efficiency of the electron-vibrational exchange mechanism [2].

To obtain an expression for the VT- and VV'-relaxation times, the approximated expression for τ has the form

$$\tau = A(T/10{,}000)^n \exp(Bt + ct^2 + d/T), \quad \mu\text{sec}\cdot\text{atm}, \tag{2.1}$$

where $t = T^{-1/3}$; A, n, B, c, and d are the approximating coefficients. At low temperatures ($T < 10{,}000$ K), it was required that the expression for τ describe the known experimental results, and, at high temperatures, the SSH-theory [3].

The specific values of the coefficients A, n, B, c, and d were determined by minimizing the difference between curve (2.1) on the one hand and the experiment and the SSH-theory on the other. The results of this approximation are presented in Table 1 for the temperature range from 200 to 100,000 K, where M is a collision partner for the VT-processes and $\Delta\tau$ is the mean deviation of the approximating curve from the experimental data and SSH-theory. For each specific M, the approximation with expression (2.1) was performed in two variants: by using five parameters (A, n, B, c, and d) and three parameters (A, n, and B). We took the well-known, generalized results of White–Millikan [4] as experimental data on the values of τ at low temperatures. For the case of N_2 and O_2 relaxation due to collision with the O atoms, Table 1 also presents the results of approximation with the experimental data taken from [7, 8]. For the case of $N_2(v) + N_2$ and $O_2(v) + O_2$ relaxation, the experimental results of [5, 6] were used. The VV'-exchange times for the N_2–NO and NO–O_2 pairs were taken from [9].

For comparison of the results obtained, Fig. 1 presents the vibrational relaxation time of the $O_2(v)$ molecules after collision with N_2 (μsec·atm). Here, 1 refers to the calculation using the White–Millikan formula, 2 to the results of [1] at $T > 10{,}000$ K, 3 to approximation by expression (2.1) with the parameters A, n, and B, 4 to approximation with the parameters A, n, B, c, and d, and 5 to the relaxation time $\tau = \tau_M + \tau_m$ suggested by Park, where τ_M is the relaxation time calculated from the White–Millikan formula and τ_m the mean time of free path [10].

At high temperatures, vibrational relaxation of N_2 can occur due to collision with an electron and the charged N_2^+, O_2^+, NO^+, N^+, and O^+ particles. Under these conditions, one can neglect the influence of attraction of the collision with the charged particles and assume the efficiency of charged particles to be identical to that of neutral particles. The role of the charged particles in the VT-relaxation of the O_2 molecules is negligible, inasmuch as the O_2 concentration is close to zero at the moment the ions and electrons appear.

When the vibrational relaxation is incomplete, the disassociation rate constant depends not only on the translational temperature T but also on the vibrational temperature T_V. According to the β-model, we

TABLE 1

Process	M	A	n	B	c	d	$\Delta\tau$	Reference
VT: $N_2(v) + M \to$ $\to N_2 + M$	N_2	$1.03 \cdot 10^{-7}$	2.79	358.9	−173.0	−692	0.12	[4, 6]
		$2.42 \cdot 10^{-6}$	2.06	281.9	—	—	0.15	
	O_2	$7.6 \cdot 10^{-11}$	4.56	480.1	283.3	−4929	0.16	[4]
		$1.59 \cdot 10^{-7}$	2.60	321.4	—	—	0.35	
	NO	$1.2 \cdot 10^{-11}$	4.92	537.7	−194.6	−3489	0.16	[4]
		$1.63 \cdot 10^{-7}$	2.60	319.2	—	—	0.35	
	N	$1.20 \cdot 10^{-8}$	3.44	339.4	804.4	−6350	0.18	[4]
		$1.03 \cdot 10^{-7}$	3.00	306.7	—	—	0.29	
	O	$1.4 \cdot 10^{-10}$	4.33	473.5	−102.7	−3752	0.16	[4]
		$1.28 \cdot 10^{-6}$	2.09	267.4	—	—	0.35	
	O	$5.22 \cdot 10^{-9}$	0.59	32.4	773.0	−2866	0.14	[7]
		$3.63 \cdot 10^{-9}$	0.39	76.3	—	—	0.29	
	e	$9.8 \cdot 10^{-19}$	5.83	63.7				
VT: $O_2(v) + M \to$ $\to O_2 + M$	N_2	$4.9 \cdot 10^{-10}$	4.81	403.1	310.4	−5330	0.1	[4]
		$2.14 \cdot 10^{-6}$	2.64	230.2	—	—	0.32	
	O_2	$8.6 \cdot 10^{-10}$	4.87	383.8	554.0	−6056	0.09	[4]
		$1.41 \cdot 10^{-6}$	2.88	241.9	—	—	0.32	
	O_2	$3.68 \cdot 10^{-8}$	3.96	311.2	494.8	−4479	0.03	[5]
		$3.14 \cdot 10^{-6}$	2.73	231.7	—	—	0.17	
	NO	$1.9 \cdot 10^{-11}$	5.45	496.1	−292.2	−3748	0.13	[4]
		$1.57 \cdot 10^{-6}$	2.69	235.7	—	—	0.37	
	N	$4.00 \cdot 10^{-9}$	4.48	359.7	246.6	−4750	0.12	[4]
		$8.50 \cdot 10^{-6}$	2.52	199.4	—	—	0.3	
	O	$8.7 \cdot 10^{-10}$	5.12	354.9	1029.0	−8502	0.11	[4]
		$2.20 \cdot 10^{-6}$	2.88	222.4	—	—	0.41	
	O	$2.80 \cdot 10^{-7}$	1.01	−161.7	2617.0	−8918	0.15	[8]
		$8.6 \cdot 10^{-11}$	2.41	117.1	—	—	0.16	
VV': N_2–O_2		$6.51 \cdot 10^{-2}$	−0.77	64.5	—	—		[9]
N_2–NO		$8.51 \cdot 10^{-3}$	0.5	69.0	—	—		[9]
NO–O_2		$9.73 \cdot 10^{-3}$	0.5	48.0	—	—		[9]

Note. The last columns gives references for measurements of the times of VT- and VV-relaxation, which are used in approximating by expression (2.1).

present the dissociation rate constant in the form [6]

$$K(T, T_V) = K^0(T) \frac{1 - \exp(-\Theta/T_V)}{1 - \exp(-\Theta/T)} \exp[-(D - \beta T)(1/T_V - 1/T)],$$

where $K^0(T)$ is the equilibrium value of the dissociation rate constant in a two-temperature gas; D is the dissociation energy. The expression e^*_{ik} entering in (1.1) for the dissociation reaction has the form $e^*_{ik} = (D - \beta T)/\Theta$.

At low temperatures, the β-model with a constant value describes well the experimental data: $\beta = 1.5$ (for the O_2 molecules) and $\beta = 3.0$ (for the N_2 molecules) [5, 6]. However, at high temperatures ($T > D/\beta$) the β-model with a constant value of β cannot describe the system satisfactorily. In particular, taking into account the CV-process in the equations of vibrational relaxation leads, in numerical calculation, to incorrect values of the vibrational temperatures T_{Vi} because of the negative values of e^*_{ik}. In this connection, we used

TABLE 2

Reaction	K_j			K_{-j}			M
	$\log A$	n	E_a, kcal/mole	$\log A$	n	E_a, kcal/mole	
$\mathrm{N}+\mathrm{N}+M \rightarrow \mathrm{N_2}+M$	21.217	−1.80	2.142	22.98	−1.92	224.93	$\mathrm{N_2}$, $\mathrm{O_2}$, NO $\mathrm{N_2^+}$, $\mathrm{O_2^+}$, $\mathrm{NO^+}$
	20.222	−1.40	0.556	22.29	−1.60	224.93	N, O, $\mathrm{N^+}$, $\mathrm{O^+}$
	18.914	−1.35	0.213	19.908	−1.28	224.93	e
$\mathrm{O}+\mathrm{O}+M \rightarrow \mathrm{O_2}+M$	19.723	−1.46	0.841	19.38	−1.09	118.0	$\mathrm{O_2}$, $\mathrm{O_2^+}$
	16.38	−0.69	−0.66	19.38	−1.09	118.0	$\mathrm{N_2}$, NO, $\mathrm{N_2^+}$, $\mathrm{NO^+}$
	16.38	−0.69	−0.66	19.896	−1.09	118.0	N, O, $\mathrm{N^+}$, $\mathrm{O^+}$
	−28.39	8.47	21.094	−25.0	7.9	140.6	e
$\mathrm{N}+\mathrm{O}+M \rightarrow \mathrm{NO}+M$	16.81	−0.5	0	15.72	0	149.68	$\mathrm{N_2}$, $\mathrm{O_2}$, $\mathrm{N_2^+}$, $\mathrm{O_2^+}$
	16.81	−0.5	0	16.86	0	149.68	NO, N, O $\mathrm{NO^+}$, $\mathrm{N^+}$, $\mathrm{O^+}$
	8.207	1.58	5.297	9.67	1.355	156.04	e
$\mathrm{N_2}+\mathrm{O_2} \rightarrow \mathrm{NO}+\mathrm{NO}$	12.85	0	110.51	11.233	0.09	66.64	
$\mathrm{N_2}+\mathrm{O} \rightarrow \mathrm{NO}+\mathrm{N}$	13.833	0	75.506	13.279	0	0	
$\mathrm{O_2}+\mathrm{N} \rightarrow \mathrm{NO}+\mathrm{O}$	9.806	1.0	6.259	9.749	1.0	41.37	
$\mathrm{N}+\mathrm{O} \rightarrow \mathrm{NO^+}+\mathrm{e}$	7.193	1.43	61.883	18.14	−0.45	0.117	
$\mathrm{N}+\mathrm{N} \rightarrow \mathrm{N_2^+}+\mathrm{e}$	8.196	1.38	131.74	20.26	−0.93	0.39	
$\mathrm{O}+\mathrm{O} \rightarrow \mathrm{O_2^+}+\mathrm{e}$	9.384	0.87	157.4	22.59	−1.62	0.08	
$\mathrm{N}+\mathrm{e} \rightarrow \mathrm{N^+}+2\mathrm{e}$	13.255	0.6	335.35	19.417	−0.5	−13.24	
$\mathrm{O}+\mathrm{e} \rightarrow \mathrm{O^+}+2\mathrm{e}$	12.716	0.68	313.91	22.0	−1.04	−9.03	
$\mathrm{O}+\mathrm{N^+} \rightarrow \mathrm{O^+}+\mathrm{N}$	5.53	1.58	0	8.667	0.96	24.213	
$\mathrm{NO}+\mathrm{e} \rightarrow \mathrm{NO^+}+\mathrm{e}$	23.81	−1.68	213.34	33.292	−3.34	0.832	
$\mathrm{N_2}+\mathrm{e} \rightarrow \mathrm{N_2^+}+\mathrm{e}$	−7.66	5.04	359.33	5.176	2.56	4.862	
$\mathrm{O_2}+\mathrm{e} \rightarrow \mathrm{O_2^+}+\mathrm{e}$	−13.0	6.02	278.48	−2.027	3.84	6.912	
$\mathrm{O_2^+}+\mathrm{N_2} \rightarrow \mathrm{O_2}+\mathrm{N_2^+}$	12.996	0	80.871	14.158	−0.44	0.755	
$\mathrm{NO^+}+\mathrm{N_2} \rightarrow \mathrm{NO}+\mathrm{N_2^+}$	15.58	0	145.51	17.167	−0.72	1.522	
$\mathrm{O_2^+}+\mathrm{N} \rightarrow \mathrm{O_2}+\mathrm{N^+}$	13.94	0.14	56.828	10.196	0.98	−4.035	
$\mathrm{O_2^+}+\mathrm{O} \rightarrow \mathrm{O_2}+\mathrm{O^+}$	12.602	−0.09	35.766	11.993	0.13	−0.884	
$\mathrm{O^+}+\mathrm{N_2} \rightarrow \mathrm{O}+\mathrm{N_2^+}$	11.954	0.36	45.303	13.714	−0.3	1.84	
$\mathrm{NO^+}+\mathrm{O} \rightarrow \mathrm{NO}+\mathrm{O^+}$	13.26	0	99.608	13.083	−0.06	−0.914	
$\mathrm{NO^+}+\mathrm{O_2} \rightarrow \mathrm{NO}+\mathrm{O_2^+}$	13.38	0.41	64.778	13.809	0.13	0.906	
$\mathrm{NO^+}+\mathrm{NO} \rightarrow \mathrm{N_2}+\mathrm{O_2^+}$	8.511	0	23.739	10.556	−0.37	3.747	
$\mathrm{NO^+}+\mathrm{NO} \rightarrow \mathrm{O_2}+\mathrm{N_2^+}$	11.041	0	102.39	14.246	−0.81	2.283	
$\mathrm{N_2^+}+\mathrm{O} \rightarrow \mathrm{NO}+\mathrm{N^+}$	14.26	0	51.189	9.827	1.0	−3.962	
$\mathrm{NO^+}+\mathrm{N} \rightarrow \mathrm{N_2}+\mathrm{O^+}$	13.53	−1.08	25.434	12.883	−0.85	−0.688	
$\mathrm{NO^+}+\mathrm{N} \rightarrow \mathrm{N_2^+}+\mathrm{O}$	13.86	0	70.539	14.978	−0.43	0.951	
$\mathrm{NO^+}+\mathrm{O} \rightarrow \mathrm{N^+}+\mathrm{O_2}$	12.0	0.5	153.4	10.771	0.68	−1.858	
$\mathrm{NO^+}+\mathrm{O} \rightarrow \mathrm{O_2^+}+\mathrm{N}$	12.89	0.29	96.568	15.405	−0.37	2.176	
$\mathrm{N_2}+\mathrm{N^+} \rightarrow \mathrm{N_2^+}+\mathrm{N}$	12.0	0.5	24.241	17.137	−0.83	6.058	
$\mathrm{O^+}+\mathrm{e} \rightarrow \mathrm{O}+h\nu$	11.029	−0.52	0				
$\mathrm{N^+}+\mathrm{e} \rightarrow \mathrm{N}+h\nu$	11.029	−0.52	0				

Note. $K_j = AT^n \exp(-E_a/RT)$, где $R = 0.001987$ kcal/(mole·K). In calculating the rate constants in reactions with electrons, one should take as temperature the electron temperature T_e. The last two reactions in the table connected with emission are taken from [11].

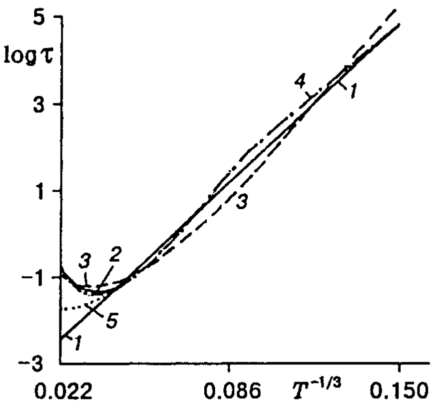

Fig. 1

the temperature dependence of β obtained by Gordiets (see formula in [1]), which is free from the above shortcoming.

The equilibrium value of the dissociation rate constant $K^0(T)$ for the N_2 and O_2 molecules has the form

$$K^0(T) = A \cdot 10^{16} \exp(-D/T)[1 - \exp(-\Theta/T)].$$

The values of the parameter A with different collision partners are presented in Table 3.

For calculating the value of Q^i_{CV} due to the recombination of the N_2 and O_2 molecules, it was assumed, in accordance with [2], that $e^*_{ik} = D/(2\Theta) - 1/2$.

3. Determination of the Optimal Mechanism of Leading Processes in Physicochemical Kinetics. The challenge of analysis of the mechanism of a complex chemical reaction is to determine the influence of separate stages of the process on the formation of kinetic curves and to build a hierarchy of stages of a complex chemical process using preset criteria. In most cases, it is very convenient to work with a compact mechanism of a chemical process, which comprises the most important stages. The procedure of ranging (building a hierarchy) of chemical reactions according to their importance makes solution of the problem possible.

For quantitative estimation of the hierarchy of reactions, one can use the local (global) sensitivity analysis [12]. To calculate the sensitivity coefficients of the type $\alpha_{ij} = \partial c_i/\partial K_j$ (c_i is the concentration of components in the mixture and K_j is the reaction rate constant of the jth process), it is necessary to integrate numerically $m+1$ times the initial system of kinetic and gas-dynamic equations (m is the number of reactions under consideration) or to determine the quantities α_{ij} by solving once a special Cauchy problem for $n(m+1)$ differential equations [12]. When the number m of reactions and the number n of components is large, the total computer time required for calculation of the sensitivity coefficients can be considerable.

However, even by solving the direct kinetic problem only once, the hierarchy of stages of a complex chemical process can be built through comparison of the reaction rates. In this case, it makes sense to introduce the following quantities [13]:

$$g_j = \int_{x_0}^{x_1} W_j\, dx \Big/ \sum_{k=1}^{m} \int_{x_0}^{x_1} W_k\, dx, \qquad g'_j = \max_x W_j \Big/ \sum_{k=1}^{m} \max_x W_k, \qquad x \in [x_0, x_1].$$

Here, W_j is the rate of the jth process, which is equal to $K_j/(\rho u) \prod_{k=1}^{m} (\rho c_k)^{\nu^+_{jk}}$; x_0 and x_1 are the initial and final integration points. The expressions for g_j and g'_j can be written similarly, the time t being the argument. It is easy to see that the quantity g_j characterizes the integral contribution of the reaction j to the total chemical transformations and g'_j characterizes the maximum contribution of the reaction over the course of

TABLE 3

Molecule	M	A
O_2	O_2	2.2
	O	7.8
	N_2, NO, N	0.36
N_2	N_2, O_2, NO	3.2
	N, O	7.1

the process development.

The quantity g_j'' is also of interest. It determines the contribution of reactions at the initial stage of the process (for instance, the nucleation reaction). For a quantitative characterization of g_j'' one may consider the quantities

$$g_j'' = W_j^0 \Big/ \sum_{k=1}^{m} W_k^0, \qquad \text{or} \qquad g_j'' = \int\limits_{x_0}^{x_0+\Delta x} W_j\,dx \Big/ \sum_{k=1}^{m} \int\limits_{x_0}^{x_0+\Delta x} W_k\,dx,$$

where W_j^0 is the rate of the jth reaction at the initial point $x = x_0$; Δx is a small increment of the argument: $\Delta x \ll |x_1 - x_0|$.

We further consider an arbitrary functional $\varphi(x, \mathrm{c}, G)$ which depends (aside from the argument x) on the concentrations of the components $\mathrm{c} = (c_1, c_2, \ldots, c_n)$ and on the gas-dynamic variables $G = (T, p, \rho, u)$. There can be more than one functional; therefore, as the functional φ one can take the vector $\varphi = (\varphi_1, \varphi_2, \ldots)$. For the sake of definiteness we assume from here on that $\varphi_i > 0$. The notion of the optimal mechanism of leading reactions, which describes the system adequately in the sense of satisfactory determination of the values of the functional φ, can be formulated as follows. It is necessary to determine a subset of the initial set of reactions that satisfy the condition

$$|\varphi^0(x, \mathrm{c}, G) - \varphi^*(x, \mathrm{c}, G)| \leqslant \varepsilon |\varphi^0(x, \mathrm{c}, G)|. \tag{3.1}$$

Here, ε is the given accuracy; φ^0 is the functional for the initial complete set of reactions and φ^* is the functional for the subset of reactions. The mechanism will be thought to be optimal if any further procedure of excluding reactions from consideration results in violating inequality (3.1).

In the algorithm we have designed, the procedure of choosing the optimal mechanism of leading processes can be divided into three stages.

Stage I. As the reaction weight, we consider the quantity p_j calculated in the form

$$p_j = g_j + r' g_j' + r'' g_j'',$$

where r' and r'' (fixed numerical coefficients) are the algorithm parameters. Written in such a form, the value of the reaction weight p_j contains information about the contribution of the reaction both at the initial point and throughout the process, and for $r' \neq 0$, regions with maximum contribution are taken into account. Aptly chosen values of the parameters r' and r'' can accelerate considerably the procedure of determining the optimal mechanism (although the algorithm also works when $r' = r'' = 0$). Special numerical studies have shown the following values to be the most appropriate from the viewpoint of reduction of the calculation time: $r' \sim 0.01$–0.1 and $r'' \sim 0.001$–0.01. The same values of r' and r'' seem to be advisable for other problems too.

First, to determine p_j, we integrate the initial system of m reactions, memorize the values of φ at the points x of interest, and calculates the values of p_j. Then the reactions can be arranged according to the decreasing weight p_j. We introduce a new numeration of reactions in the initial base of reactions according to the decrease of p_j, i.e., in the new numeration of reactions $p_1 \geqslant p_2 \geqslant p_3 \geqslant \ldots \geqslant p_{m+1} \geqslant p_m$. Let R_j denote the set of renumerated reactions numbered from 1 to j (R_m is the complete base of reactions).

Then we integrate the equations, taking into account the first $m_1 = 2^k$ reactions from the new list (k is the greatest integer such that $2^k < m$). If criterion (3.1) holds for the first m_1 reactions, we consider the first m_2 reactions where $m_2 = m_1 - 2^{k-1}$. If (3.1) does not hold, then $m_2 = m_1 + 2^{k-1}$ $(m_2 < m)$. The procedure is further repeated for sets of m_q reactions

$$m_q = m_{q-1} \pm 2^{k-(q-1)} \qquad (m_q < m).$$

For $m_q \geqslant m$, we proceed to the next step with respect to q.

Defining m_q in such a way, we will determine in $k+1$ steps the first m_{k+1} reactions $R^{(1)} = R_j$ $(j = m_{k+1})$ that do not violate criterion (3.1). Thus, the first stage makes it possible to exclude from consideration those reactions whose contribution to the total chemical transformations is small.

Naturally, the sequence of reactions in the hierarchy is different from the sequence obtained on the basis of ranging the sensitivity coefficients $\partial\varphi/\partial K_j$, but generally speaking in both cases the group of reactions whose contribution is insignificant will be at the end of the list, i.e., when p_j is small, so is $\partial\varphi/\partial K_j$. For the same reason, the system $R^{(1)}$ can contain a reaction (or a group of reactions) that can be excluded without violation of criterion (3.1). These "redundant" reactions are selected at stages II and III.

Stage II. If the number of reactions and components after stage I are denoted by $m_{(1)}$ and $n_{(1)}$, the computer time reduction after stage I is estimated to be $m_{(1)}n_{(1)}^2/mn^2$ (the fact that the computer time is proportional to the number n of components is due to the necessity of calculating the Jacobi matrix in the STIFF package [12]). In most problems the author considered, the computer time was reduced by a factor of two through several tens. This simplifies significantly the practical implementation of stages II and III (see below).

At stage II, the reactions from $R^{(1)}$ are excluded in groups, depending on whether criterion (3.1) holds. The principle by which the groups are determined is not rigorously specified. We chose a variant in which pairs of the direct and reverse reactions contained in the system $R^{(1)}$ are considered groups. Denote by $R^{(2)}$ the set of reactions after stage II.

Stage III. Depending on whether or not criterion (3.1) holds, each reaction from $R^{(2)}$ is excluded or put back into $R^{(2)}$. We denote by $R^{(3)}$ the optimal mechanism of the leading processes obtained after stage III.

The content of the mechanism $R^{(3)}$ can strongly depend on the specific form of the functionals φ_i $(i = 1, 2, \ldots)$, accuracies ε_i $(i = 1, 2, \ldots)$, initial conditions for the concentrations of the components c_i, and gas-dynamic variables $G = (T, p, \rho, u)$. Note also that in the program designed the choice of the optimal mechanism of leading reactions, including all the stages, is automatic. The set of reactions $R^{(3)}$ obtained after termination of the algorithm (along with the reaction rate constants K_j) is saved in a separate file so that it can be used in further calculations.

Naturally, the number of kinetic equations under consideration can be decreased further using the Dalton law, the material balance relations of conservation of chemical elements, and the law of conservation of charge. Such a reduction in the number of equations can also be performed if it is possible to single out quasiequilibrium blocks in the system that allow the differential equations to be replaced by algebraic ones (transcendental, in the general case). In some cases, it is possible to reduce the number of independent kinetic equations by singling out the "basic" components in the system [14].

The above treatment of the problem is not quite strict, since the rate constants for chemical reactions are determined with an error at present. For processes with a small contribution, such uncertainty in the rate constants can be of little consequence in terms of satisfaction of criterion (3.1), while for the leading reactions a change in the reaction rate constants can lead to a change in the content of the resulting mechanism $R^{(3)}$. A way out of this situation can be suggested. Let us change randomly the temperature dependence of the rate constants of the processes within the given error range. For each new set of constants, we determine its own optimal mechanism $R^{(3)}$. With a sufficient number of trials, the union of all $R^{(3)}$ represents the optimal mechanism with account of the uncertainties in the rate constants of the processes. The random points in the space of the reaction rate constant K_j must be generated according to a specific error distribution function. If a system takes into account both direct and reverse reactions, it is enough to generate the rate constants only for the direct reaction, and the rate constant for the reverse reaction can be calculated by using the

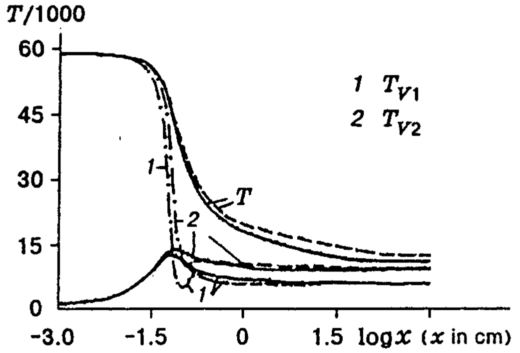

Fig. 2

equilibrium constant. As the error distribution function, one can take either a uniform distribution between the minimum and maximum values of the constant, or a normal distribution with parameters set in advance.

The algorithm for choosing an optimal mechanism of physicochemical processes in gas has been considered for the case of chemical reactions. The addition of vibrational relaxation equations does not complicate the procedure from the formal mathematical point of view. But if the processes proceed simultaneously, the amount of information contained in the quantities p_j is different for chemical reactions and for vibrational relaxation processes. Thus it makes sense, in choosing the mechanism, to construct two independent hierarchies of processes and to determine the optimal mechanism of leading processes parallel in each subsystem.

4. Mechanism of Processes in High-Temperature Air. The described model of kinetics of the processes was realized for the case of one-dimensional flow behind the front of a normal shock wave in a nonviscous gas.

The initial system of equations for the gas parameters behind the normal shock-wave front has the form

$$\rho u = \text{const}, \quad p + \rho u^2 = \text{const}, \quad \sum c_i h_i + \sum R_0 \Theta_i c_i e_i + u^2/2 = \text{const}, \quad p = R_0 \rho T \sum c_i,$$

where p, T, ρ, and u are the pressure, temperature, density, and the gas flow velocity; R_0 is the universal gas constant; h_i is the enthalpy of the ith component (neglecting the energy of vibrational modes). The kinetic equations for e_i and c_i are presented above. It was assumed that the gas-dynamic variables p, T, ρ, and u underwent a jump in the shock-wave front, whereas the initial concentrations of the components and vibrational temperatures did not change. It was also assumed that the shock wave propagated in a channel with a constant cross section so that behind the shock wave the kinetic equations for e_i and c_i were integrated together with gas-dynamic equations under the assumption that $\rho u = \text{const}$.

Figure 2 presents the distributions of the translational temperature T and the vibrational temperatures of oxygen T_{V1} and of nitrogen T_{V2} behind the shock wave propagating at a velocity of 11 km/sec in the atmosphere at an altitude H of 70 km (the pressure and the temperature ahead of the shock wave were $5.2 \cdot 10^{-5}$ atm and 217 K), depending on the distance x from the wave (the solid curves refer to a calculation with the complete initial set of chemical reactions, VT-, VV'-, and CV-processes presented in Section 2). Immediately behind the front the values of the two-temperature dissociation rate constant $K(T, T_V)$ for the O_2 and N_2 molecules are small and hence the vibrational temperatures T_{Vi} grow mainly due to the VT-process. The dissociation process starts after excitation of vibrations and the values of the vibrational temperatures are henceforth determined by competition of the VT- and CV-processes. Allowance for the CV-process changes qualitatively the pattern of vibrational temperature alteration; in actual fact, quasiequilibrium between the translational and vibrational temperatures is not attained but is attained between the VT- and CV-processes. This can also be seen from Fig. 2, where the dotted curves refer to the vibrational temperatures obtained under the assumption that the formal equality $Q^i_{VT} + Q^i_{CV} = 0$ holds. Though there is, in all appearance, no

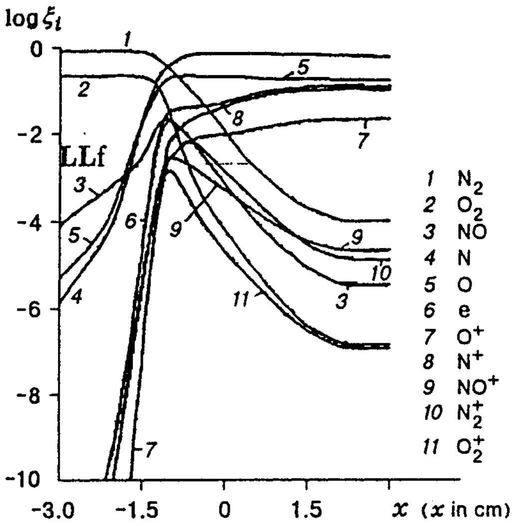

Fig. 3

physical meaning in these values of vibrational temperatures, they allow one to determine the distance x behind the shock after which one can assume that quasiequilibrium between the VT- and CV-processes has been attained. The presence of minima in the dotted curves is due to the following. The dissociation rate constant (at real values of the temperatures T and T_V) has a maximum in the vicinity of the vibrational-temperature maximum, and because of the intense CV-process the value of the vibrational temperature obtained from the formal equality $Q^i_{VT} + Q^i_{CV} = 0$ becomes smaller than the true value of the vibrational temperature T_{Vi}. Then the value of $K(T, T_V)$ diminishes with x (because of the fall in the translational temperature) and quasiequilibrium is established simultaneously.

From the moment the quasiequilibrium is established the values of vibrational temperatures remain practically at the same level. This makes it possible to determine the concentrations c_i of the components behind the normal shock wave by using one-temperature kinetics wherein constant values of T_{Vi} are substituted for the vibrational temperatures in the dissociation rate constants for the O_2 and N_2 molecules (see [1]). But for greater accuracy in determining the translational temperature T and vibrational temperature T_{Vi} the VT-and CV-processes must be taken into account (see below).

The above algorithm for determining the leading processes has been used to obtain the mechanism in the case where the translational and vibrational temperatures were taken as the functionals φ_i. If one takes $\varepsilon = 0.2$ to be the allowable error for T and $\varepsilon = 0.15$ for T_{Vi}, the optimal mechanism consists of the following reactions and processes:

$N_2 + M \rightarrow 2N + M$ $(M = N,\ O,\ N_2)$, $O_2 + M \rightarrow 2O + M$ $(M = O,\ O_2)$, $NO + M \rightarrow N + O + M$ $(M = N,\ O)$,
$O + N_2 \leftrightarrow N + NO$, $N + N \leftrightarrow N_2^+ + e$, $N_2 + N^+ \rightarrow N_2^+ + N$, $N^+ + 2e \rightarrow N + e$, $N_2^+ + O \rightarrow NO + N^+$,

$$\begin{array}{lll} VT: & N_2(v) + M \rightarrow N_2 + M & (M = N,\ O,\ N_2,\ O_2), \\ VT: & O_2(v) + M \rightarrow O_2 + M & (M = N_2,\ O_2,\ O), \\ CV: & N_2(v) + M \rightarrow 2N + M & (M = N,\ O,\ N_2,\ O_2), \\ CV: & O_2(v) + M \rightarrow 2O + M & (M = O,\ O_2). \end{array} \tag{4.1}$$

The dotted curves in Fig. 2 correspond to the temperature values for the mechanism (4.1).

The distributions of the molar fractions ξ_i of neutral components for an electron and charged particles (with a complete mechanism of chemical reactions, VT-, VV-, and CV-processes from Section 2) are presented in Fig. 3 for $v = 11$ km/sec and $H = 70$ km.

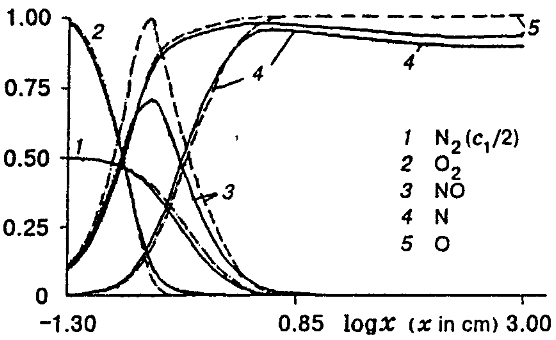

Fig. 4

Using a one-temperature kinetics model that was obtained from the two-temperature model under the assumption of T_{Vi} = const, we found the mechanism of the leading reactions determining the concentration of the neutral components N_2, O_2, NO, N, and O.

Condition (3.1) for the above components has the form

$$|c_i^0 - c_i| \leqslant \begin{cases} \varepsilon c_i^0, & \text{if} \quad c_i \geqslant 0.1 \max c_i^0, \\ \varepsilon \cdot 0.1 \max c_i^0, & \text{if} \quad c_i < 0.1 \max c_i^0, \end{cases} \tag{4.2}$$

where c_i^0's are the concentrations of the components with a complete set of reactions. With condition (3.1) written in this form, most attention in seeking the mechanism is given to the accurate determination of large values of c_i.

It turned out that behind a normal shock wave ($v = 11$ km/sec and $H = 70$ km) at a relative accuracy of $\varepsilon = 0.4$ it was sufficient to use the following reactions for determining the concentrations of the neutral particles

$$\begin{gathered} \mathrm{O_2} + M \to 2\mathrm{O} + M \quad (M = \mathrm{O},\ \mathrm{O_2}), \quad \mathrm{NO} + M \to \mathrm{N} + \mathrm{O} + M \quad (M = \mathrm{N_2},\ \mathrm{O},\ \mathrm{N}), \\ \mathrm{O} + \mathrm{N_2} \to \mathrm{N} + \mathrm{NO}, \quad \mathrm{N} + \mathrm{O_2} \to \mathrm{O} + \mathrm{NO}, \quad \mathrm{O_2} + \mathrm{N_2} \to 2\mathrm{NO}. \end{gathered} \tag{4.3}$$

Figure 4 presents the distributions of the concentrations c_i (in relative units) with the complete set of reactions from Table 2 (the solid curves) and with reactions (4.3) (the dotted curves) at $v = 11$ km/sec and $H = 70$ km.

The search for the optimal mechanism with condition (4.2) for the neutral and charged particles requires extending system (4.3) with the reactions

$$\begin{gathered} \mathrm{N_2} + M \to 2\mathrm{N} + M \quad (M = \mathrm{N_2},\ \mathrm{N}), \quad \mathrm{N} + \mathrm{N} \leftrightarrow \mathrm{N_2^+} + \mathrm{e}, \quad \mathrm{N} + \mathrm{O} \leftrightarrow \mathrm{NO^+} + \mathrm{e}, \quad \mathrm{N^+} + \mathrm{O} \leftrightarrow \mathrm{N} + \mathrm{O^+}, \\ \mathrm{O_2^+} + \mathrm{e} \leftrightarrow 2\mathrm{O}, \quad \mathrm{N_2^+} + \mathrm{O} \to \mathrm{NO} + \mathrm{N^+}, \quad \mathrm{N_2} + \mathrm{N^+} \to \mathrm{N_2^+} + \mathrm{N}, \quad \mathrm{NO^+} + \mathrm{N_2} \to \mathrm{NO} + \mathrm{N_2^+}. \end{gathered} \tag{4.4}$$

If the relative accuracy for all components is reduced to $\varepsilon = 0.2$, one must add to processes (4.3) and (4.4) the following reactions to calculate concentrations with the above accuracy:

$$\mathrm{NO^+} + \mathrm{O} \leftrightarrow \mathrm{O_2^+} + \mathrm{N}, \quad \mathrm{N_2^+} + \mathrm{O} \to \mathrm{N_2} + \mathrm{O^+}, \quad \mathrm{O^+} + 2\mathrm{e} \to \mathrm{O} + \mathrm{e}, \quad \mathrm{N^+} + \mathrm{e} \to \mathrm{N} + h\nu, \quad \mathrm{N^+} + \mathrm{O_2} \to \mathrm{N} + \mathrm{O_2^+}.$$

Thus, the results presented indicate that it is possible to simplify significantly the mechanism of physicochemical processes in the gas. Such a reduction in the number of the reactions used makes it possible to reduce considerably the computer time without impairing the adequacy.

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