ISOTOPE SEPARATION IN NONEQUILIBRIUM REACTIONS INVOLVING THE OXIDATION OF NITROGEN MOLECULES IN SUPERSONIC NOZZLES

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The effect of isotope separation during chemical reactions that take place under thermodynamically nonequilibrium conditions, which was first reported in [1], has been investigated repeatedly in recent years in theoretical and experimental studies [2-5]. In the experiments the vibration excitation of the reactant (N_2 or CO) necessary for occupancy of the upper vibrational levels of the molecules by the heavy isotope and for overcoming the energy threshold of the reaction was provided by an electrical discharge. The coefficients of nitrogen-isotope separation in the reaction products (K_{NO} = 1.02-1.5) measured in the latter studies [2-3] were found to be much lower than predicted by the thoery. It was indicated that the reason for the low separation effect may be the nonselective channels of production of the nitrogen oxides in the discharge, resulting from the ionization, dissociation, and electronic excitation of the molecules by the electrons. It seems possible to reduce substantially the role of the nonselective channels of the NO production, obtaining a vibrationally excited reactant by equilibrium heating of the nitrogen with subsequent cooling in a supersonic nozzle.

In [4] it was shown by a computational method that the reactions of oxidation of vibrationally excited molecules of nitrogen at not-too-high translational temperatures begin to take place only after the establishment of a quasistationary distribution of N_2 molecules over the vibrational levels; the reaction yield, the separation coefficient K_{NO}, and the time τ_v required to establish a quasistationary distribution of molecules over the vibrational levels increase as the translational temperature decreases. Consequently, in the separation of nitrogen isotopes during oxidation reactions taking place in a supersonic flow, it is desirable to widen the latter only so long as τ_v remains less than the time of flow of the gas in the supersonic part of the nozzle.

The purpose of the present study is to investigate the quantitative dependence of the yield of the nitrogen oxidation reaction in a supersonic flow and the corresponding values of K_{NO} on the parameters of deceleration of the flow and the geometry of the nozzle.

It is assumed that nitrogen, after equilibrium heating to a temperature T_0 at pressure p_0, flows out through a supersonic nozzle with a given geometry and that at a distance a from the critical cross section a quantity of partially dissociated oxygen is mixed with the flow. The mixing was assumed to be instantaneous. It was further assumed that the flow of oxygen was much less than the flow of nitrogen and that therefore when the two gases were

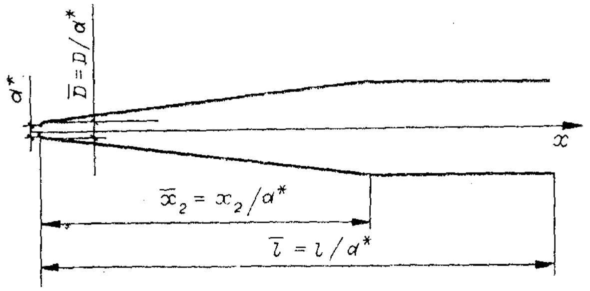

Fig. 1

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TABLE 1

No.	Reaction	lg*A*	*n*	*E*, kcal	ΔT, °K	Reference
1	$N + O_2 \rightarrow NO + O$	13,00	0	7,5	300—3000	[11]
2	$N + NO \rightarrow N_2 + O$	13,44	0	0,5	280—1900	[11]
3	$N + N + Ar \rightarrow N_2 + Ar$	14,70	0	—1	90—611	[12]
4	$N + O + N_2 \rightarrow NO + N_2$	16,83	—0,5	0	300	[13[
5	$N + O + O_2 \rightarrow NO + O_2$	16,29	—0,5	0	300	[13]
6	$N + O_3 \rightarrow NO + O_2$	11,53	0	0	300	[14]
7	$N + N_2O \rightarrow NO + N_2$	⩾13,70	0	0	298	[11]
8	$N + NO_2 \rightarrow N_2O + O$	12,67	0	0	298	[11]
9	$N + NO_2 \rightarrow NO + NO$	12,55	0	0	298	[11]
10	$N + NO_2 \rightarrow N_2 + O_2$	⩽12,43	0	0	298	[11]
11	$N + NO_2 \rightarrow N_2 + O + O$	11,83	0	0	298	[11]
12	$N + N + N_2 \rightarrow N_2 + N_2$	14,70	0	—1	90—6400	[11]
13	$N + N + N_2O \rightarrow N_2 + N_2O$	15,34	0	0	298	[11]
14	$O + O + Ar \rightarrow O_2 + Ar$	21,95	—2,9	0	196—327	[14]
15	$O + O + N_2 \rightarrow O_2 + N_2$	17,41	—0,93	0	300—7500	[11]
16	$O + O + O_2 \rightarrow O_2 + O_2$	15,99	—0,41	0	300—6000	[11]
17	$O + NO + Ar \rightarrow NO_2 + Ar$	15,00	0	—1,5	200—500	[15]
18	$O + NO + O_2 \rightarrow NO_2 + O_2$	21,43	—2,04	0	212—2300	[11]
19	$O + NO + N_2 \rightarrow NO_2 + N_2$	15,18	0	—1,9	200—500	[15]
20	$O + NO + N_2O \rightarrow NO_2 + N_2O$	15,79	0	—1,2	298—473	[15]
21	$O + O_2 + Ar \rightarrow O_3 + Ar$	12,52	0	—2,3	180—1000	[11]
22	$O + O_2 + N_2 \rightarrow O_3 + N_2$	12,97	0	—1,7	303—863	[11]
23	$O + O_2 + O_2 \rightarrow O_3 + O_2$	13,09	0	—1,09	300—1000	[11]
24	$O + O_2 + O_3 \rightarrow O_3 + O_3$	13,78	0	—0,6	343—373	[11]
25	$O + NO \rightarrow NO_2 + h\nu$	12,39	—2,01	0	212—3750	[15]
26	$O + NO_2 + N_2 \rightarrow NO_3 + N_2$	17,00	0	0	300	[11]
27	$O + O_3 \rightarrow O_2 + O_2$	12,79	0	4,31	269—409	[16]
28	$O + N_2O \rightarrow N_2 + O_2$	10,48	0	14,5	876—1031	[17]
29	$O + N_2O \rightarrow NO + NO$	11,00	0	15,5	876—1031	[11]
30	$O + N \rightarrow NO + h\nu$	7,72	—0,35	0	300—1300	[11]
31	$O_3 + O_3 \rightarrow O_2 + O_2 + O_2$	12,65	0	18,8	343—373	[11]
32	$N_2 + O_2 \rightarrow NO + NO$	24,96	—2,5	128,5	1400—4300	[11]
33	$NO_2 + NO_2 \rightarrow NO + NO + O_2$	12,61	0	26,91	473—1020	[11]
34	$NO_2 + NO_2 \rightarrow NO_3 + NO$	11,89	0	23,90	473—703	[11]
35	$N + O + Ar \rightarrow NO + Ar$	15,47	0	0	300	[11]
36	$NO + O_2 + NO_2 \rightarrow NO_3 + NO_2$	7,32	0	—1,0	473—703	[11]
37	$NO + N_2O \rightarrow NO_2 + N_2$	14,30	0	50,0	1500—2200	[11]
38	$N_2O + N_2 \rightarrow N_2 + O + N_2$	13,10	0	44,0	1300—1950	[18]
39	$NO_3 + NO_3 \rightarrow NO_2 + NO_2 + O_2$	12,41	0	7,70	550—1100	[11]
40	$NO_2 + NO_2 + N_2 \rightarrow N_2O_4 + N_2$	13,23	0	1,70	250—350	[15]
41	$NO_2 + NO_2 \rightarrow N_2O_4$	11,70	0	0	298	[15]
42	$O_3 + NO_2 \rightarrow NO_3 + O_2$	10,86	0	4,90	220—340	[15]
43	$NO + O_3 \rightarrow NO_2 + O_2$	11,83	0	2,45	198—322	[11]
44	$O + NO_2 \rightarrow NO + O_2$	13,01	0	0,60	280—550	[15]

mixed, the thermodynamic and gasdynamic properties of the main flow did not change. The gas was considered to be ideal, and the flow one-dimensional. The effects of viscosity and heat conduction were ignored. To find the parameters characterizing the isotope separation during reactions involving the oxidation of vibrationally excited molecules in a supersonic flow, we must solve a system of equations of relaxation kinetics and chemical kinetics. In formulating the equations we assumed that the concentrations of the NO, N_2O, NO_2, N_2O_4, and O_3 molecules were less by several orders of magnitude than the concentrations of N_2 and O_2 molecules, so that their influence on the relaxation kinetics was disregarded. We considered vibrational—vibrational exchange between the molecules of $N^{14}N^{14}(V)$, $N^{14}N^{15}(V)$, and $O_2(V)$ and vibrational—translational relaxation of these molecules themselves by themselves and the atoms of N and O. The chemical reactions between the components of the mixture, written in the form $K = AT^n e^{-E/RT}$ cm³/(mole•sec), are shown in Table 1. Thus, the system of differential equations for determining the occupancies of the vibrational levels of the molecules $N^{14}N^{14}$, $N^{14}N^{15}$, and O_2 and the concentration of the chemical reactants has the following form:

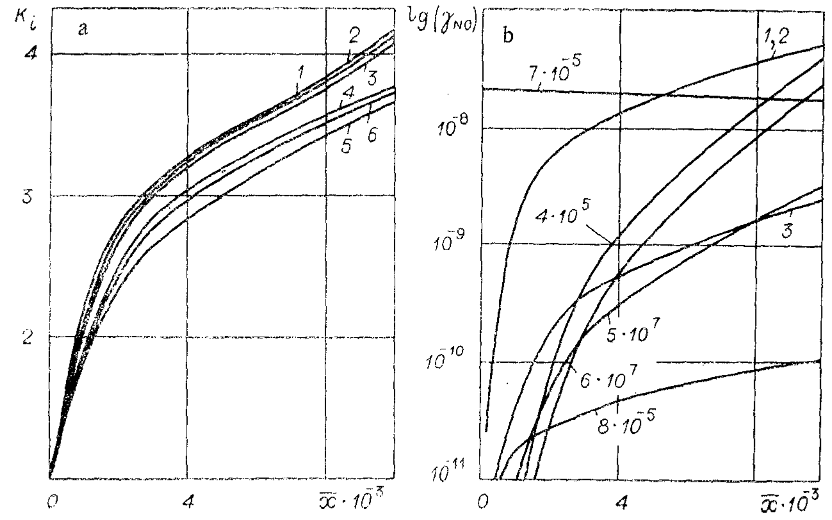

Fig. 2

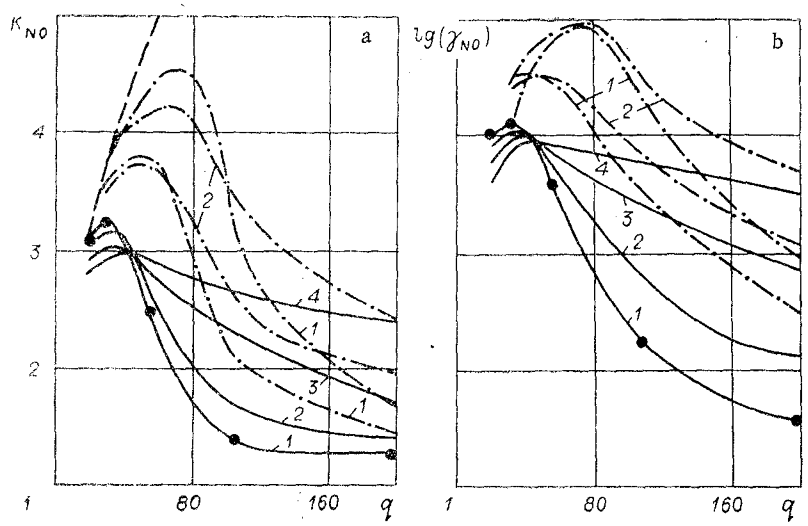

Fig. 3

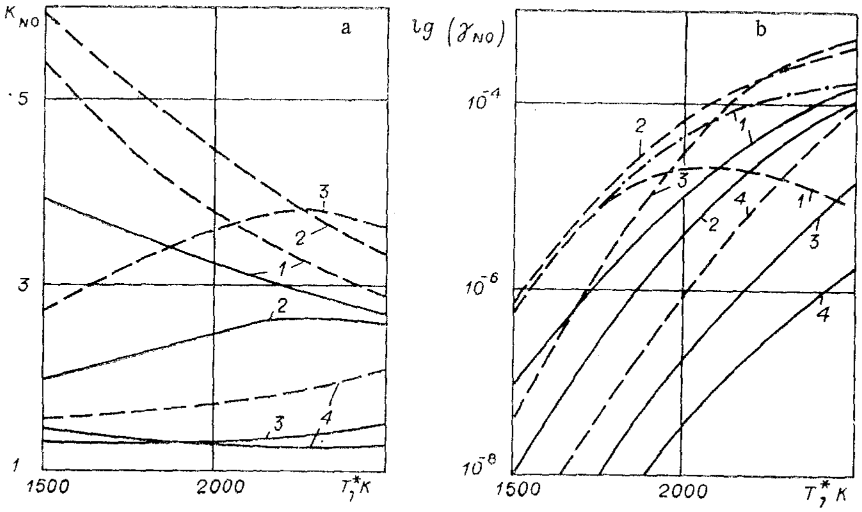

Fig. 4

$$\frac{dM(V)}{dx} = \left(\frac{dM(V)}{dx}\right)_{VV} + \left(\frac{dM(V)}{dx}\right)_{VT} + \left(\frac{dM(V)}{dx}\right) + \frac{M(V)}{\rho}\frac{d\rho}{dx}, \quad \frac{dR}{dx} = \left(\frac{dR}{dx}\right)_{\text{chem}} + \frac{R}{\rho}\frac{d\rho}{dx}, \tag{1}$$

where M = $N^{14}N^{14}$, $N^{14}N^{15}$, O_2; R = $N^{14}O$, $N^{15}O$, $N^{14}O_2$, $N^{15}O_2$, $N^{14}N^{14}O$, $N^{14}N^{15}O$, $N^{14}O_3$, $N^{15}O_3$, $N^{14}N^{14}O_4$, $N^{14}N^{15}O_4$, O_3, N^{14}, N^{15}, O, Ar; V = 0, 1, ..., 18.

The expression for the term $\frac{1}{\rho}\frac{dp}{dx}$ can be obtained from the conservation equations and the equations of state for an ideal gas [4].

Figure 1 shows the geometric profile of the nozzle investigated in calculating the parameters of the separation of the nitrogen isotopes. The nozzle consists of three sections: spherical, conical, and cylindrical.

In performing the calculations, we endeavored to make them suitable to the purpose, and therefore we were forced to impose restrictions on the deceleration parameters and the nozzle geometry. We were guided by the data of [6] and usually took $p_0 \leq 10^7$ Pa, $T_0 < 2500$°K. $l/d^* = 1000$, $d^* = 1$ mm. Here l is the length of the nozzle and d^* is the diameter of the critical cross section.

The solution of the system of equations (1) was carried out by numerical integration using Gear's method [7]. The average calculation time for one variant on the EC-1033 computer was about 30 min. As a result of the calculation, we found values for the occupancies of the isotopic modifications of the molecules N_2 and O_2 according to vibrational levels, the values of the concentrations of the chemical components, and also the temperature T, the pressure p, the density ρ, and the velocity v as functions of the coordinate x along the axis of the nozzle. The separation parameters K_{NO} and K_{NO_2} for the principal products of the chemical reactions of the NO and the NO_2 were determined as follows:

$$K_{NO} \equiv ([N^{15}O]/[N^{14}O])/K_0, \quad K_{NO_2} \equiv ([N^{15}O_2]/[N^{14}O_2])/K_0,$$

where $K_0 = {}^1/_{273}$ is the natural ratio between the isotopes N^{15} and N^{14}. The separation parameters K_N, K_{N_2O}, K_{NO_3}, $K_{N_2O_4}$ were found in an analogous manner.

Figure 2a and Fig. 2b show the distribution of the separation parameters K_i and the mole fractions γ_i of the chemical reactants along the nozzle axis for $T^* = 1500$°K, $p^* = 37 \cdot 10^5$ Pa, $[N_2]_0 = 99.604\%$, $[O_2]_0 = 0.198\%$, $[O]_0 = 0.198\%$, $\overline{a} = 5$, $\overline{D} = 3.8$, $\overline{x}_2 = 400$, $\alpha = 0.1°$ (1 - NO; 2 - N; 3 - NO_2; 4 - N_2O; 5 - NO_3; 6 - N_2O_4; 7 - O; 8 - O_3). The superscript * relates to the parameters at the critical cross section. As can be seen from Fig. 2, during the time the gas flows in the nozzle the separation parameters do not reach their maximum values because the characteristic time of alignment of the quasiequilibrium functions for the distribution over the vibrational levels of the isotopic modifications of the nitrogen molecules exceeds the characteristic time of flow of the gas in the nozzle. Since τ_V decreases with increasing vibrational and translational temperatures, while the separation coefficient decreases, it may happen that the separation parameters are not single-valued functions of the deceleration temperature and the nozzle geometry.

In Fig. 3a, b we show the variation of K_{NO} and log (γ_{NO}) as functions of the degree of widening of the nozzle, $q = S/S^*$, for different values of the length of the conical widening section $\overline{x}_2$ (1 - 50; 2 - 200; 3 - 500; 4 - 1000) for $T^* \simeq 2000$°K, $p^* = 37 \cdot 10^5$ Pa, $[N_2]_0 = 97.672\%$, $[O_2]_0 = 0.194\%$, $[O]_0 = 0.194\%$, $[O_3]_0 = 1.94\%$, $\overline{a} = 5$, D = 3.8. It is characteristic that for fixed deceleration parameters of the nitrogen and a given total length of the nozzle, there is an optimal degree of widening for which the separation coefficient K_{NO} and the NO yield of the reaction, γ_{NO}, simultaneously take on their maximum values. The existence of maxima is attributable to the fact that, on the one hand, as q increases, there is a decrease in the translational temperature of the gas, which leads to an increase in K_{NO} and γ_{NO}, and, on the other hand, a decrease in the translational temperature and the pressure leads to a "freezing" of the chemical and relaxation processes. Thus, an increase in the degree of widening of the nozzle beyond the optimal value is tantamount to a decrease in the effective length of the nozzle.

For low degrees of widening ($q \leq 50$) the values of K_{NO} and γ_{NO} are weakly dependent on the length of the widening section and increase only slightly as $\overline{x}_2$ decreases. For $q > 50$ the decrease in $\overline{x}_2$ leads to a substantial decrease in K_{NO} and γ_{NO}. It should be noted that for a nozzle of length $l = 1$ m the maximum values of $K_{NO} \approx 3.2$ and $\gamma_{NO} \approx 1.3 \cdot 10^{-5}$ are attained when $q \approx 30$, which corresponds to a translational temperature of the gas in the

TABLE 2

No.	$[N_2]_0$, %	$[O_2]_0$, %	$[O]_0$, %	$[O_3]_0$, %	$T^*=1500$ K				$T^*=2000$ K			
					K_{NO}	[NO], %	K_{NO_2}	$[NO_2]$, %	K_{NO}	[NO], %	K_{NO_2}	$[NO_2]$, %
1	99,6026	0,1978	0,1978		4,08	$5{,}0851\cdot10^{-6}$	4,02	$4{,}8420\cdot10^{-6}$	3,08	$8{,}5325\cdot10^{-4}$	3,05	$8{,}0388\cdot10^{-4}$
2	99,8018	—	—	0,1982	4,15	$6{,}5405\cdot10^{-13}$	3,78	$2{,}8246\cdot10^{-13}$	3,34	$1{,}0553\cdot10^{-7}$	3,10	$5{,}3819\cdot10^{-8}$
3	99,8018	—	0,1982	—	4,08	$5{,}0906\cdot10^{-6}$	4,01	$4{,}9427\cdot10^{-6}$	3,08	$8{,}3931\cdot10^{-4}$	3,05	$8{,}1259\cdot10^{-4}$
4	97,8627	1,9430	0,1943	—	4,03	$5{,}1956\cdot10^{-6}$	3,97	$4{,}2876\cdot10^{-6}$	3,06	$9{,}1295\cdot10^{-4}$	3,03	$6{,}7616\cdot10^{-4}$
5	99,7821	0,1981	0,0198	—	4,19	$3{,}3289\cdot10^{-6}$	3,91	$3{,}3455\cdot10^{-6}$	3,26	$4{,}4550\cdot10^{-4}$	3,09	$4{,}3532\cdot10^{-6}$
6	99,7821	0,0198	0,1981	—	4,08	$5{,}0793\cdot10^{-6}$	4,02	$4{,}9161\cdot10^{-6}$	3,07	$8{,}3854\cdot10^{-4}$	3,05	$8{,}0947\cdot10^{-4}$
7	97,8627	0,1943	1,9430	—	3,67	$4{,}7477\cdot10^{-6}$	3,67	$2{,}8526\cdot10^{-6}$	2,89	$1{,}0015\cdot10^{-3}$	2,88	$6{,}9826\cdot10^{-4}$
8	97,6729	0,1939	0,1939	1,9393	4,06	$8{,}4487\cdot10^{-6}$	3,97	$3{,}9405\cdot10^{-7}$	3,08	$1{,}0952\cdot10^{-3}$	2,98	$6{,}4237\cdot10^{-5}$

TABLE 3

	K_{NO}			ν_{NO}		
T_{KO_2} / $\overline{x}_2$	500	1000	200	500	1000	2000
50	2,52	2,52	2,49	$5{,}00\cdot10^{-6}$	$5{,}05\cdot10^{-6}$	$5{,}09\cdot10^{-6}$
100	2,64	2,64	2,65	$5{,}92\cdot10^{-6}$	$5{,}96\cdot10^{-6}$	$6{,}20\cdot10^{-6}$
200	2,74	2,74	2,73	$6{,}77\cdot10^{-6}$	$6{,}65\cdot10^{-6}$	$6{,}95\cdot10^{-6}$
500	2,85	2,85	2,86	$7{,}92\cdot10^{-6}$	$7{,}96\cdot10^{-6}$	$8{,}17\cdot10^{-6}$
750	2,90	2,91	2,92	$8{,}71\cdot10^{-6}$	$8{,}72\cdot10^{-6}$	$8{,}95\cdot10^{-6}$
1000	2,94	2,95	2,95	$9{,}28\cdot10^{-6}$	$9{,}31\cdot10^{-6}$	$9{,}50\cdot10^{-6}$

nozzle of T = 370°K. For comparison with the stationary case, in Fig. 3 we show by a dashed curve the variation of K_{NO} as a function of the initial translational temperature corresponding to the translational temperature of the gas in the cylindrical part of the nozzle. The initial vibrational temperature was taken to be 2000°K. We can clearly see how much the separation parameters fall short of their maximum values. As the braking pressure increases (the dot-and-dash curves; $p_0 = 17.5 \cdot 10^6$; $35 \cdot 10^6$ Pa), the separation parameters approach their maximum possible values, and the optimal values of q are shifted into the region of high values.

The results given above were obtained for a fixed initial composition of the gas. In order to find out how strongly the initial gas composition affects the separation parameters, we performed a series of calculations with variation of the gas composition for the following nozzle geometry: $\bar{D} = 3.8$, $\bar{x}_2 = 400$, $\alpha = 0.1°$, $\bar{a} = 5$. The pressure at the critical cross section is $p^* = 37 \cdot 10^5$ Pa, and the initial temperature of the injected dissociating oxygen is $T_{O_2} = 500°K$. The results of the calculation are summarized in Table 2, where columns 2-4 show the initial gas composition in percent by volume and columns 6-13 show the separation parameters for the two temperatures $T^* = 1500$ and 2000°K. It follows from Table 2 that varying the composition of the injected gas has little effect on the separation coefficients, since within the framework of the assumption we have made, there is no substantial change in the thermodynamic parameters of the flow, which determine the formaton of the distribution functions and consequently determine the separation coefficient of the nitrogen isotopes. We must conclude that the amount of atomic oxygen in the injected gas has a greater influence on the separation parameters than the amount of oxygen or ozone. This is attributable not only to the high chemical activity of the atomic oxygen and to its participation in the selective chain process of formation of nitrogen oxide $O + N_2(V) \rightarrow NO + N$, $O_2(V) + N \rightarrow NO + O$, but also to the strong relaxation of nitrogen and oxygen by the atoms of oxygen [4].

The increase in the relative fraction of atomic oxygen leads to a decrease in the separation coefficient K_{NO}, and the NO yield of the reaction passes through the optimum value. The substantial decrease (by several orders of magnitude) in the NO yield of the reaction in the case when pure ozone is mixed with the nitrogen is easily understood if we consider that in this case the chain process of nitrogen-oxide formation is limited by the process of decomposition of ozone with the formation of molecular and atomic oxygen, which at low temperatures takes place very inefficiently.

To explain the effect of the vibrational excitation of the molecular oxygen on the separation parameters, we performed calculations for the cases $T_{O_2} = 1000$ and 2000°K. The other conditions in this case correspond to the conditions of Fig. 3 for q = 50. For convenience in comparison, the results of the calculations for $T_{O_2} = 500$, 1000, and 2000°K are summarized in Table 3. It can be seen that the vibrational temperature of the oxygen has practically no effect on the separation coefficient K_{NO} and that only the NO yield of the reaction increases slightly (no more than 3%) as T_{O_2} increases from 500 to 2000°K.

In the present study we used a model of instantaneous mixing. Actually, complete mixing of the flows takes place some distance away from the injection cross section. This can unquestionably have an effect on the results of the calculation. To assess the influence of the finite rate of mixing of the flows on the separation parameters, we performed calculations in which we varied the distance from the critical cross section to the injection point $\bar{a}$. The dots in Fig. 3 indicate the values of K_{NO} for $\bar{a} = 100$. It can be seen that moving the injection point within reasonable limits has little influence on the final result of the calculation. Physically this is attributable to the fact that the separation coefficient K_{NO} and the NO yield of the reaction, γ_{NO}, are determined mainly by the formation of distribution functions of the isotopic modifications of the molecules at the higher vibrational levels ($V \geq 10$), which takes place chiefly in the final part of the nozzle. It was assumed that the oxygen is added to the flow of N_2, in which the translational temperature of the nitrogen is sufficiently low to ensure that the nonselective processes of nitrogen-oxide formation will be inefficient.

In [4] we found a relation for the separation parameters of the isotopes of nitrogen in the products of oxidation of the vibrationally excited molecules of nitrogen at low translational temperatures when the reaction took place in a closed constant volume. According to [4], the value of K_{NO} increases with decreasing initial vibrational temperature for a fixed initial translational temperature, while the NO yield of the reaction decreases. The numerous calculations for the parameters of separation of nitrogen isotopes when the

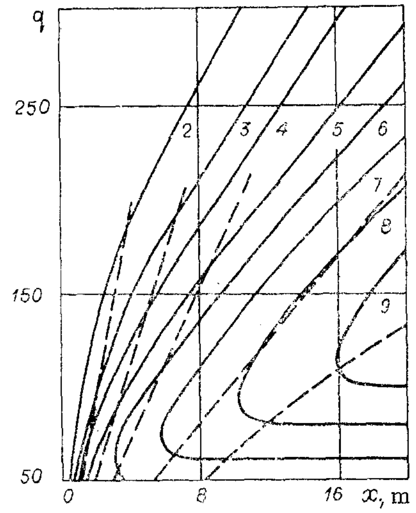

Fig. 5

gas flows in a supersonic nozzle of finite length which we carried out in the present study showed that in this case we do not observe a single-valued relation between the initial temperature of the gas and the separation coefficient K_{NO}. This is clearly illustrated by the curves in Fig. 4 which show the variation of K_{NO} and γ_{NO} as functions of the critical temperature T* for different degrees of widening q(1 - 30; 2 - 50; 3 - 100; 4 - 200). The length of the conical section is $\bar{x}_2 = 50$, and the solid curves correspond to $p^* = 37 \cdot 10^5$ Pa, while the dashed curves correspond to $18.5 \cdot 10^6$ Pa. The remaining parameters are the same as in Fig. 3. It can be seen that, depending on the geometry of the nozzle, the values of K_{NO} either decrease or increase with increasing T*. For low degrees of widening, when τ_V is close to the time of flow of the gas in the nozzle, the function giving K_{NO} in terms of T* is single-valued and analogous to the function given in [4]. As the pressure increases with decreasing τ_V, the nature of the function giving K_{NO} in terms of T* may change (see curves 2).

Unlike the variation of the separation coefficient as a function of the critical temperature, the variation of the reaction yield as a function of T* is single-valued. As T* increases, the value of γ_{NO} increases. The nonmonotonic variation of log (γ_{NO}) as a function of T* when q = 30 and $p^* = 18.5 \cdot 10^6$ Pa can be attributed to the complete oxidation of the NO, with transition to NO_2, when the temperatures and pressures are high. In this case, unlike the others shown in Fig. 4, the main product of the chemical reaction will be NO_2 molecules. The dot-and-dash curve indicates the total NO + NO_2 yield of the reaction.

In choosing the working temperature, we must take account of the fact that we are usually interested not only in obtaining isotopes with a given degree of enrichment but also in obtaining a sufficient quantity of product. Consequently, when $p^* = 37 \cdot 10^5$ Pa, it is desirable to work at T* = 2300-2500°K and a degree of widening of 30-50. When the temperature does down to 1500°K, the value of K_{NO} will increase (for q = 30) by only 30%, while the yield will decrease by a factor of about 10^3.

In the general case, for each specific installation, depending on its technical possibilities and the purpose of the operation, a specific range of operating temperatures may be found.

For the limitations we imposed on the gas braking parameters and the length of the nozzle, the best results obtainable under these conditions are $K_{NO} \simeq 3.2$ when $\gamma_{NO} \simeq 1.3 \cdot 10^{-5}$. To increase the separation parameters, we should increase the braking pressure and the nozzle length with a view to reducing τ_V in comparison with the time of gas flow in the nozzle. As the calculations showed, increasing p_0 to $35 \cdot 10^6$ Pa at T* = 2000°K enables us to increase K_{NO} to 4.5 and the yield γ_{NO} to 10^{-4}.

In Fig. 5, in the coordinates (q, l), we show the curves corresponding to K_{NO} = const for T* = 1670°K, $p^* = 92.5 \cdot 10^5$ Pa, $x_2 = 50$, $\bar{D} = 3.8$, $\bar{a} = 5$. It should be noted that what we mean by the degree of widening q is the effective degree of widening, taking account of the correction for the displacement thickness. The estimate of the displacement thickness was made by the semiempirical formulas of [6] for a turbulent boundary layer, since the Reynolds number Re = 10^7.

In Fig. 5 the dashed curves are the graphs of the nozzle length l as a function of the degree of widening q, with the condition that the rate G_δ of gas flow through a boundary layer of thickness δ is equal to the gas flow rate at the core of the flow, G_e. The region to the left of this curve corresponds to $G_e > G_\delta$, and the region to the right corresponds to $G_e < G_\delta$. The calculation of the average-mass temperature in the boundary layer, $\langle T\rangle = \int_0^\delta T dG \Big/ \int_0^\delta dG$, at the cross section of the nozzle at which $G_e = G_\delta$ [8-10] showed that for nozzles with q = 50-200 the value of <T> is 1.5-2.5 times the temperature at the core of the flow. Since an increase in the translational temperature is accompanied by a sharp decrease in the reaction yield and the separation coefficient, this gives us reason to believe that the boundary layer does not affect the separation parameters when $G_e \geq G_\delta$.

The various dashed curves in Fig. 5 correspond to various diameters of the critical cross section of the nozzle (from left to right, d* = 1, 1.5, 2, 3, and 4 mm). As can be seen from Fig. 5, a proportional increase in the transferse nozzle dimensions, as a result of a decrease in the relative thickness of the boundary layer, is accompanied by an increase in the distance from the critical cross section of the nozzle to the cross section at which $G_e = G_\delta$. Since it is possible in this way to increase the nozzle length, with a braking pressure of $p_0 = 17.5 \cdot 10^6$ Pa, a temperature T_0 = 2000°K, a nozzle length l = 16 m, a degree of widening q = 100-150, and a critical cross-sectional diameter d* = 4 mm, we can attain K_{NO} values of 8-9 with a reaction yield of $\gamma_{NO} \simeq 8 \cdot 10^{-5}$.

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FEATURES OF VIBRATIONAL RELAXATION OF THE SYSTEM OF LOW CO_2 MOLECULE LEVELS

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By using numerical computations and analytic solutions, the vibrational relaxation of the system of low CO_2 molecule levels is studied. The examination is on the basis of level-by-level kinetics in the range of initial pressures and translational temperatures characteristic for a number of experimental papers in which the rate of energy transfer between symmetric longitudinal and deformation vibrations was determined. The nonmonotonicity of the behavior of the vibrational level populations with time is clarified and the domains of their variation are indicated in which the determination of the energy transfer rate constant is possible in the individual relaxation channels.

1. Because of the strong Fermi resonance between symmetric and deformation vibrations of CO_2 molecules, the equidistance of the energetic spectrum already turns out to be spoiled for the lowest levels. This results in anharmony of the vibrations and is the reason for the high rate of vibrational exchange between the modes ν_1 and ν_2, where ν_1 is the notation of the symmetric valence, and ν_2 of the symmetric deformation vibrations. Experimental investigations have clarified the substantial spread (more than two orders of magnitude) in the magnitude of the rate constants for this exchange, as has repeatedly been mentioned in the literature (see [1], for example). Theoretical computations of the transfer rate on the basis of the Shvarts—Slavsky—Herzfeld theory [2, 3] result in large values. Computations on the basis of taking account of long-range attractive forces in the Born approximation [4] yield a value for the transition probability of the vibrational energy between the modes ν_1 and ν_2 that is an order greater than in [2]. High theoretical values of the transfer probabilities between the modes ν_1, ν_2 would seem to permit the assumption of local equilibrium between the symmetric and deformation vibrations. However, such low values of the probability of this transfer have been obtained in a number of experimental papers, that the assumption of local equilibrium must be rejected.

On the basis of processing a set of experimental papers, a set of energy transfer constants was proposed in [5] for a system of low CO_2 molecule levels. However, here assumptions were made which significantly simplified the relaxation process; for instance, it was assumed in advance that the exchange process between Fermi-perturbed levels proceeds at the highest rate. In order to eliminate a number of a priori assumptions about the kinetics of the exchange processes between the modes ν_1 and ν_2, computations of the populations of the individual vibrational levels of the CO_2 molecules were performed in this paper on the basis of level-by-level kinetics with all the fundamental relaxation channels taken into account and by using the theoretical values of the transition probabilities taken from [3, 4].

2. The scheme for the vibrational levels of the CO_2 molecule that are henceforth considered is represented in Fig. 1. The digit 1 denotes the energy level corresponding to double the value of the energy of the level 01^10, i.e., the level with the energy 1334.9 cm^{-1}, 2 is the level with mixed wave functions $(10^00,02^00)^{I}$ because of Fermi resonance (according to the terminology in [2]), and with the energy 1285.7 cm^{-1}, 3 is the level $(10^00,02^00)^{II}$

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