

Chemical Reactions and Energy Exchange under Thermally Non-Equilibrium Conditions at High Temperatures in N₂O-CO System

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Investigations of monomolecular decomposition of N₂O in the region of uncompleted vibration relaxation were performed. Behind reflected shock wave infrared emission of CO₂ ($\lambda = 4.2 \mu\text{m}$), chemiluminescent emission CO-O ($\lambda = 364 \pm 10 \text{ nm}$) and radiation absorption at $\lambda = 200 \div 220 \text{ nm}$ (overlapped spectra of N₂O, CO₂, NO and O₂) were registered in the N₂O-CO-Ar mixture. Time-dependent profiles for CO₂ and N₂O concentrations and chemiluminescent emission CO-O intensity were obtained.

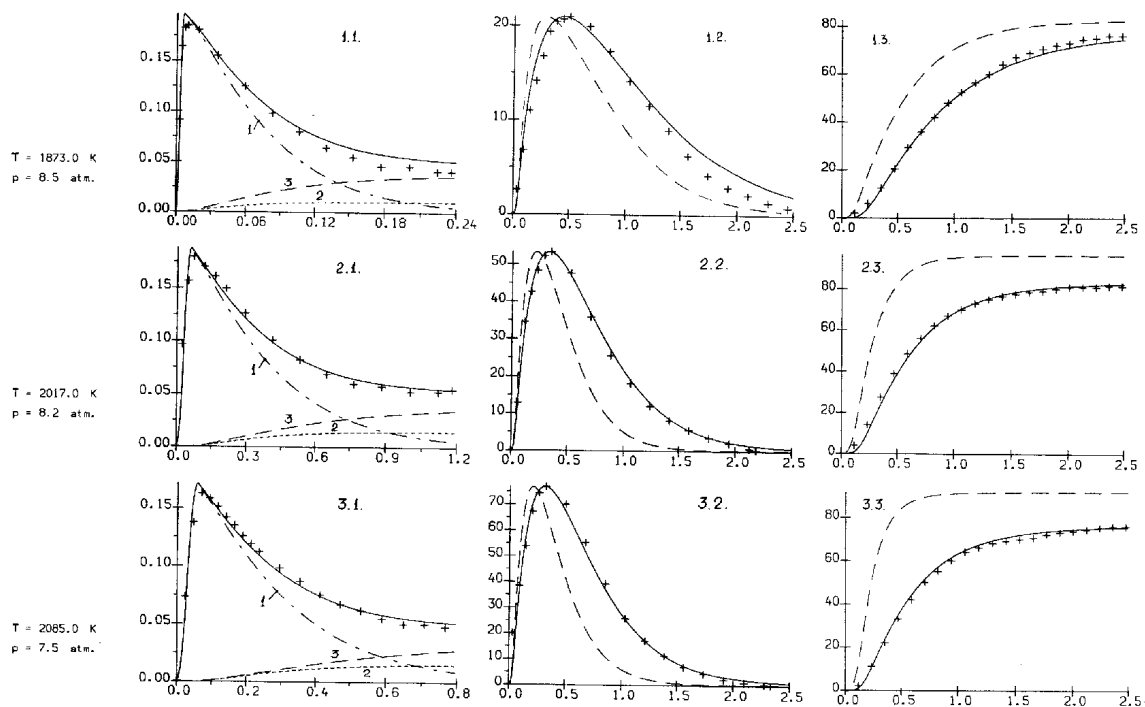


Figure 1: Measured and calculated absorption profiles in UV-range (1.1-6.1; $\lambda = 220 \text{ nm}$); chemiluminescent emission CO-O ($\lambda = 364 \pm 10 \text{ nm}$, 1.2-6.2) and IR - emission of CO₂ ($\lambda = 4.25 \pm 0.1 \mu\text{m}$, 1.3-6.3). Mixture N₂O : CO : Ar = 0.5 : 25 : 74.5. Time scale t , $\times 10^{-4} \text{ s}$.

It has been shown, that at high temperatures rate of monomolecular decomposition was determined by vibration relaxation of the mixture; the bottle-neck process of this relaxation is intermolecular energy exchange between N₂O(ν_3) and CO.

The figure 2 shows the experimentally measured chemiluminescence emission CO-O half-increase time in the mixtures N₂O : CO : Ar = 0.5 : 25 : 74.5 N₂O : CO : H₂ : Ar = 0.5 : 25 : 0.01 : 74.49.

On the same figure 2 there were also shown characteristic time of vibrational energy relaxation in the system and characteristic time of N_2O monomolecular decomposition under the thermally-equilibrium conditions.

It is clear that at high temperatures rate of N_2O decomposition, calculated with the "equilibrium" model, becomes comparable and even less than characteristic time of vibrational relaxation. In this region a significant difference between experimentally measured N_2O decomposition time and calculated with "equilibrium" model appears.

Thus, the process of monomolecular decomposition of N_2O in the binary N_2O -CO mixture is limited by vibrational energy exchange.

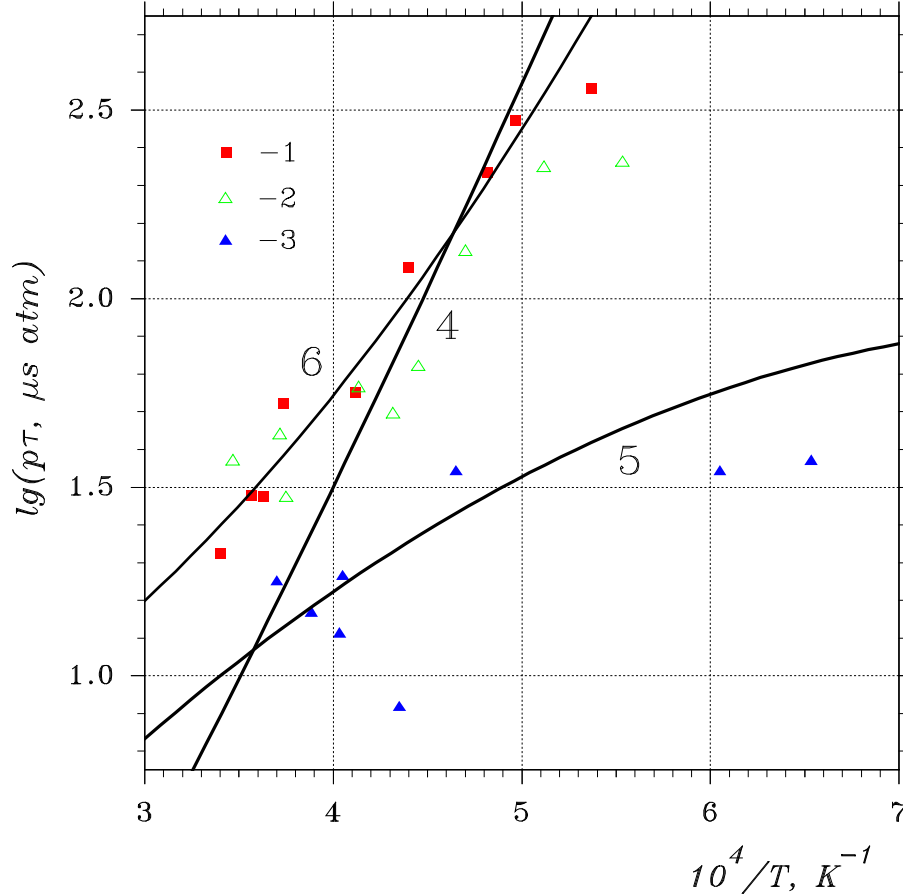


Figure 2: Dynamics of monomolecular decomposition of N_2O at high temperatures. Time of half-increase of atomic oxygen concentration: mixture 0.5% N_2O , 25%CO, Ar (points 1); mixture 0.5% N_2O , 25%CO, 0.01% H_2 , Ar (points 2). Vibrational relaxation time, mixture 0.5% N_2O , 25%CO, Ar (points 3). Curve 4 — calculation of vibrational energy relaxation time in the "mode" approximation. Curve 5 — calculation of the rate constant of monomolecular decomposition of N_2O in the mixture 0.5% N_2O , 25%CO, Ar in the thermally-equilibrium regime Curve 6 — calculation of the oxygen atoms half-increase time in the mixture 0.5% N_2O , 25%CO, Ar under thermally non-equilibrium conditions with model proposed in the present work.

The complete task of reaction mechanism development was subdivided into to sep-

arate tasks: model of vibration energy relaxation and exchange and model of chemical reactions under non-Boltzmann conditions with participation of excited reagents. For the chemical reactions modeling in N_2O -CO-Ar system level-by-level kinetics of vibration energy exchange between N_2O , NO, N_2 , O_2 , CO and CO_2 has been taken into account in the framework of SSH theory. Calculation of rate constants $k_{n,n-1}^{n'-1,n'}(T)$ and $k_{n,n-1}(T)$ was made within the frames of SSH-theory.

All the reactions in mechanism were represented as a set of "elementary" processes, dealing with reagents and products at the certain vibration states. Thereby, the problem to construct an analytical model that makes it possible to evaluate microconstants of reaction rates and a function of the level distribution of the product on the basis of experimentally measured values is going on to be actual.

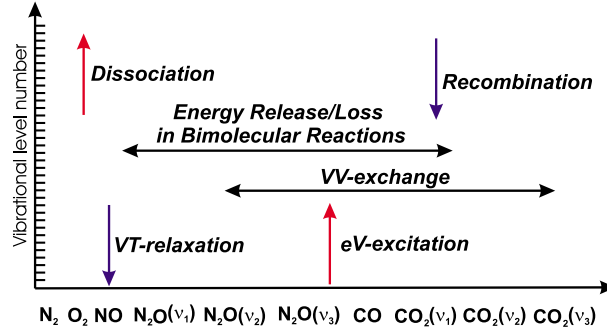
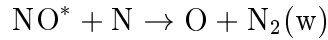
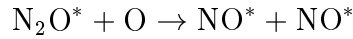
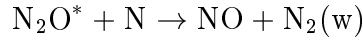
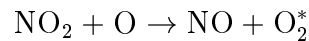
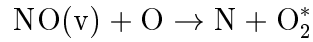


Figure 3: Scheme of energy exchanges used for vibrational kinetics analysis in N_2O , CO, CO_2 , NO, N_2 , O_2 system.

Vibrational energy distribution function for different molecules at high temperatures is determined by a number of processes of vibrational energy exchange and energy release in the reactions:



Reactions



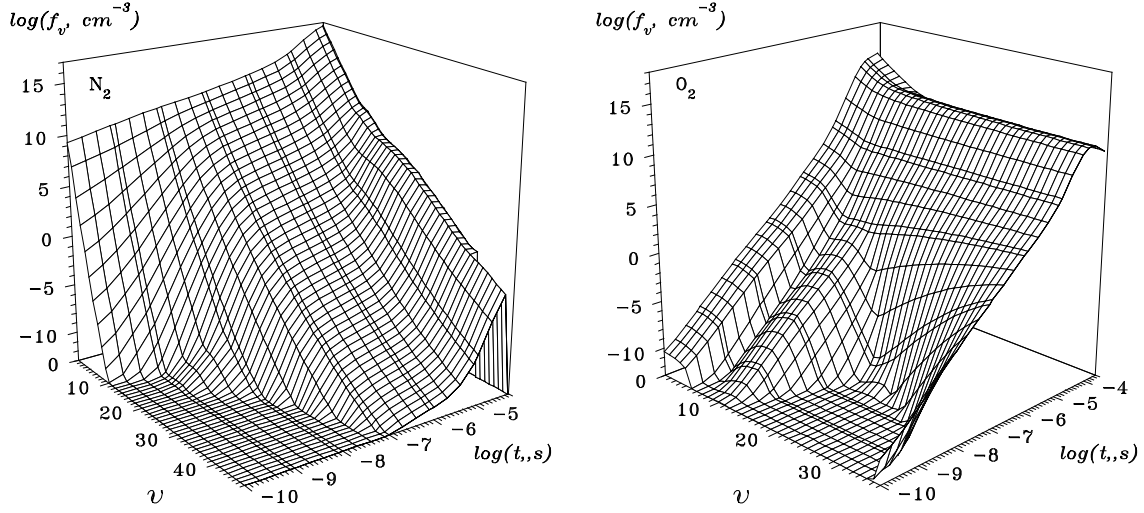


Figure 4: Vibrational energy distribution function. a) – N_2 ; b) – O_2 . Mixture 0.5% N_2O , 25% CO , Ar. $T = 2000$ K, $p = 10$ atm.

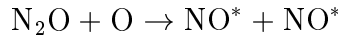
lead to non-Boltzmann EDF shape for O_2 molecules.

Vibrational relaxation of antisymmetric mode of N_2O has a significantly different mechanism in the N_2O - CO mixture with compare to the mixture N_2O -Ar (. 5).

Intramolecular VV' -energy exchange between antisymmetric and deformation and symmetric modes provides the population increase of upper vibrational levels of ν_3 -mode. From the other hand, the exchange between $\text{N}_2\text{O}(\nu_3)$ and CO depopulates excited states of antisymmetric mode N_2O .

In this case energy distribution within ν_3 -mode establishes very slowly and significant difference between vibrational temperature of deformation and antisymmetric mode established.

Vibrational energy distribution function of NO at the beginning of the process has a substantially non-Boltzmann shape due to energy release to the internal degrees of freedom in the reaction:



Dynamics of vibrational energy relaxation and monomolecular decomposition of N_2O were shown on the Figure 6. Profiles of "vibrational temperature" for different vibrational modes and N_2O , NO number densities were shown.

Dynamics of vibrational relaxation in N_2O - CO – system was determined by fast VV' – energy exchange between antisymmetric mode of N_2O and CO . Vibrational temperatures of $\text{N}_2\text{O}(\nu_3)$ and CO are close to each other during the process, and active N_2O decomposition starts after the relaxation zone.

Under low temperatures characteristic time of vibrational relaxation is far smaller than time scale of chemical processes in the thermally-equilibrium conditions (. 2). In this temperature region vibrational relaxation practically does not affect on the rate of N_2O decomposition and rate of O -atoms formation in the system (Figure 2).

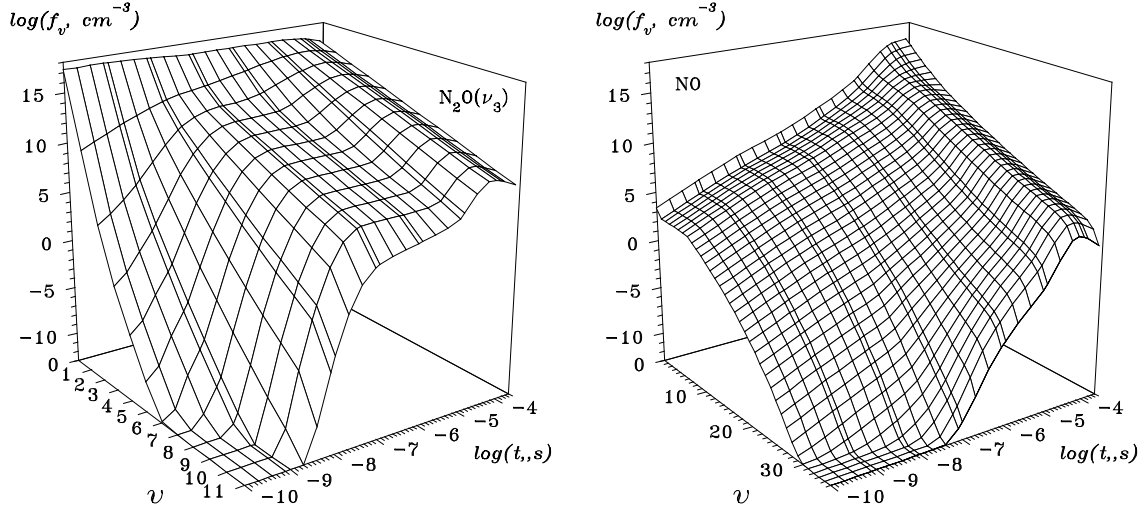


Figure 5: Vibrational energy distribution function. a) – $\text{N}_2\text{O}(\nu_3)$; b) – NO . Mixture 0.5% N_2O , 25% CO , Ar. $T = 2000$ K, $p = 10$ atm.

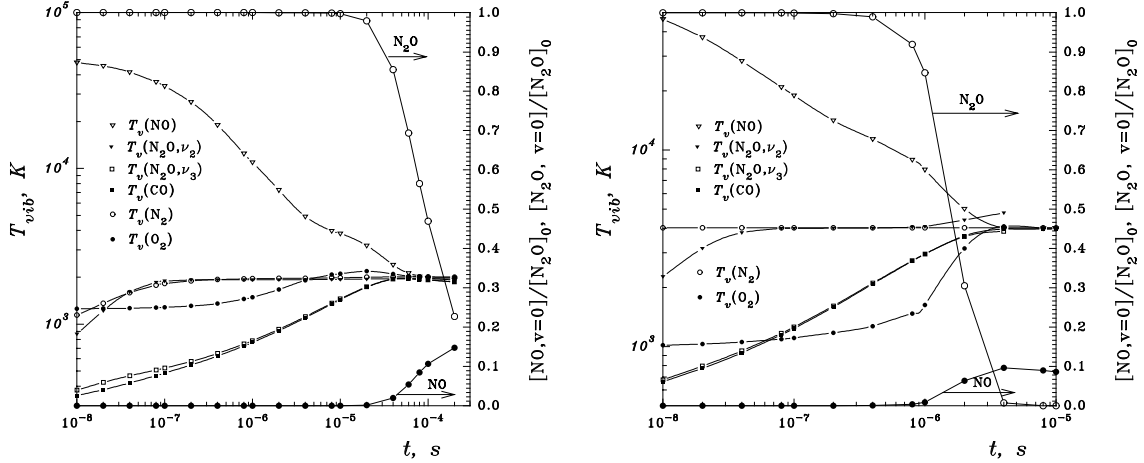


Figure 6: "Vibration temperature" and main components concentration dynamics during first stage of N_2O decomposition. Mixture 0.5% N_2O , 20% CO in Ar. $p = 10$ atm. a) – $T_{ini} = 2000$ K; b) – $T_{ini} = 4000$ K.

Chemical reactions model developed for thermally nonequilibrium regimes allows to describe the main peculiarities of the process of N_2O monomolecular decomposition in two-temperature conditions. A good agreement between the experimentally measured characteristic times for the reaction (such as a half-increase of O-atoms concentration time) and the vibration energy relaxation time was obtained.

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