# POSSIBILITY OF THE OCCURRENCE OF DISSOCIATION REACTIONS OF MULTIATOMIC MOLECULES DURING RAPID COOLING IN AN EXPANDING SUPERSONIC STREAM

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We investigate the possibility of the occurrence of the reaction involving the dissociation of $N_2O$ and the exchange reaction $N_2O + CO \rightarrow N_2 + CO_2$ during rapid cooling of a gas mixture due to supersonic expansion in a nozzle. A numerical solution of the equations for the balance of vibrational energy and the kinetics of the chemical reactions under nonequilibrium conditions is given. We find the values of the parameters that are necessary for the experimental observation of the phenomena considered.

Rapid exchange of vibrational quanta often leads to the establishment of quasiequilibrium vibrational distributions, which persist during a time t such that $\tau^{VV} < t < \tau^{VT}$, where $\tau^{VV}$ and $\tau^{VT}$ are the durations of V−V and V−T-processes respectively.

For example, in a system of oscillators A and B the relationship between the temperature $T_A$ and $T_B$

$$\theta_B/T_B = \theta_A/T_A - (\theta_B - \theta_A)/T \tag{1}$$

becomes established upon attainment of V−V equilibrium [1, 2], where $\theta_A$ and $\theta_B$ are the characteristic temperatures of the oscillators A and B, respectively, and T is the gas temperature.

Under specific conditions ($\theta_B > \theta_A$, $T_A$, $T_B \gg T$) there can be considerable pumping by oscillators with lower energy quanta from those with higher energy quanta. Under nonequilibrium conditions in a system of anharmonic oscillators, energy transfer to higher levels can result in a substantial increase in the "temperature" of these levels. The distribution of populations over the levels of an anharmonic oscillator (the term "Treanor distribution" is usually used) is described by the equation [3, 4]

$$N_n = \frac{N}{Q}\exp\left\{-n\left[\frac{\theta_1}{T_1} - (n-1)\frac{\Delta E}{T}\right]\right\} \equiv \frac{N}{Q}x_n. \tag{2}$$

Here $N_n$ is the concentration of particles at the level n, Q is the statistical sum of an anharmonic oscillator and its anharmonicity (°K), respectively, and $T_1$ is the effective vibrational temperature for the levels 1-0. As many chemical reaction rates are determined by the population of sufficiently high vibrational levels, it is of interest to consider the effect of energy transfer under nonequilibrium conditions on the occurrence of certain model reactions. In this case dissociation and exchange reactions are convenient. The dissociation rate constant is determined by the extent of vibrational excitation of the dissociating molecules. The dependence of the rate of exchange reactions on the vibrational excitation of the original reagents has apparently not been sufficiently investigated, although, in a cycle of papers by Bauer and his associates (see [5], for example), it is definitely shown that vibrational excitation plays a decisive role in a large number of exchange reactions. Experiments with molecular beams of HI and DI have indicated [6] that even for very high translational energy (from 20 to 109 kcal/mole in the center-of-mass system, i.e., higher than the activation energy) these molecules do not enter into an exchange reaction with the formation of HD if they do not have sufficient vibrational energy.

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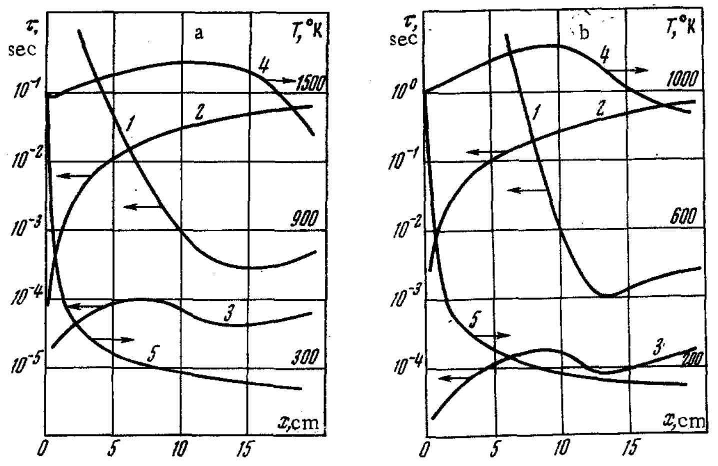

Fig. 1

Thus, if the cooling process is limited to gasdynamical methods (for example, flow in a nozzle), the factors that promote the flow of a reaction at low temperatures are the following:

1) nonresonance vibrational pumping of "working" molecules from inert diatomic molecules with long relaxation times (for instance $N_2$);

2) an increase in the population of high levels of the working molecules due to anharmonicity (see Eq. (2)). Correspondingly, a significant drop in the density during flow in a nozzle promotes a decrease in the chemical reaction rate.

Under conditions where the vibrational temperature breaks away from the translational temperature, the population having sufficiently high vibrational levels for the feasibility of distribution (2) can increase with a decrease in the translational temperature and as a result one can expect a corresponding increase in the rates of certain dissociation and exchange reactions with a decrease in the temperature.

As an item for investigation we choose the dissociation of $N_2O$ in the exchange reaction

$$N_2O + CO \rightarrow N_2 + CO_2$$

The choice of such systems is dictated by the following circumstances:

1) the main contribution to the reaction rate must be made by levels n that are low enough so that the V−T reaction does not proceed (i.e. $n < n^*$, where $n^*$ is the level at which the rates of the V−V and the V−T processes are comparable). Therefore among dissociation processes the most prominent are nonadiabatic reactions with predissociation;

2) the activation energy of the reaction $N_2O + CO$ is 23 kcal/mole according to the data of [7]; that is, for vibrational levels with such an energy $n < n^*$;

3) in molecules having a number of atoms greater than three, it is difficult to cause a breaking away of vibrational temperature from translational temperature because of the high rate of intramolecular V−V exchange;

4) as both the reactions chosen are exothermic, an acceleration of the reaction because of evolved vibrational energy can be relied upon.

The goal of the present study involves the clarification of possibilities of experimental observation of the course of dissociation and exchange reactions that take place during flow through nozzles used in combination with shock tubes.

We consider the flow of a mixture 5% $N_2O$ + 95% $N_2$ through a plane nozzle (whose height d at the critical cross section is 1 mm, whose length is 20 cm, and whose expansion angle is $\alpha \approx 12°$). To find the basic characteristics of the flow it suffices to limit ourselves to the approximate analytical relationships

$$T = T_0\left(1 + \frac{\gamma-1}{2}M^2\right)^{-1} \qquad \rho = \rho_0\left(1 + \frac{\gamma-1}{2}M^2\right)^{1/(\gamma-1)} \tag{3}$$

expressing the temperature and density of the gas in terms of the Mach number M, the ratio of specific heats $\gamma$, and the initial parameters $T_0$, $\rho_0$ at the entrance of the nozzle. In mixtures containing a small addi-

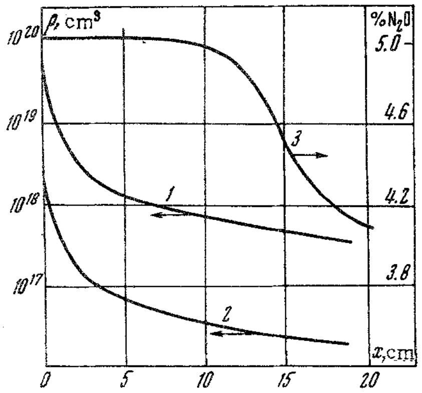

Fig. 2

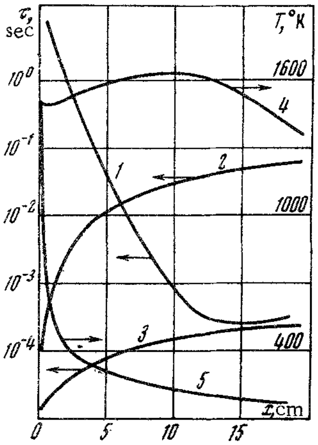

Fig. 3

tion of reacting material such an approximation is completely satisfactory. The dependence of the Mach number on distance along the nozzle is determined by solution of the equation

$$\left(\frac{F}{F_*}\right)^2=\frac{1}{M^2}\left[\frac{2}{\gamma+1}\left(1+\frac{\gamma-1}{2}M^2\right)\right]^{(\gamma+1)/(\gamma-1)}$$

where $F/F_*$ is the ratio of the running area of the transverse cross section to the area of the critical cross section.

We write down equations for the rate of change in the number of vibrational quanta occurring in the antisymmetric vibration of $N_2O$ ($\varepsilon_B$) and the vibration of nitrogen ($\varepsilon_A$) [4, 8]

$$\frac{d\varepsilon_A}{dt}=-\frac{\varepsilon_A-\overset{\circ}{\varepsilon}_A}{\tau_A^{VT}}-Q_{10}{}^{01}N_B\left[\varepsilon_A(\varepsilon_B+1)\exp\left(\frac{\theta_A-\theta_B}{T}\right)-\varepsilon_B(\varepsilon_A+1)\right]+(\varepsilon_C-\varepsilon_B)\frac{1}{N_A}\left(\frac{dN_A}{dt}\right)_C \tag{4}$$

$$\frac{d\varepsilon_B}{dt}=-\frac{\varepsilon_B-\overset{\circ}{\varepsilon}_B}{\tau_B^{VT}}+Q_{10}{}^{01}N_A\left[\varepsilon_A(\varepsilon_B+1)\exp\left(\frac{\theta_A-\theta_B}{T}\right)-\varepsilon_B(\varepsilon_A+1)\right]+(D-\varepsilon_B)\frac{1}{N_B}\left(\frac{dN_B}{dt}\right)_C \tag{5}$$

Here $\varepsilon_A{}^0$, $\varepsilon_B{}^0$ are the equilibrium values of the numbers of vibrational quanta per molecule; $\tau_A^{VT}$ and $\tau_B^{VT}$ are the vibrational-translational relaxation times of molecules A and B; $N_A$ and $N_B$ are the densities of the molecules; $\theta_A$ and $\theta_B$ are the characteristic temperatures; D is the dissociation energy; $\rho_{10}^{01}$ is the probability of an exchange of vibrational quanta between molecules A and B; and $\varepsilon_C$ is the quantity of vibrational quanta per molecule A that originate in the exothermic reaction.

Using a model based on the rapid exchange of vibrational quanta [1, 8], we obtain an equation for $\varepsilon_B$ under the condition $\varepsilon_B < 1$ with account being taken of gas temperature, chemical activation of molecules A, and dissociation of molecules B

$$\begin{gathered}\frac{d\varepsilon_B}{dt}=-(\varepsilon_B-\varepsilon_B{}^\circ)\left[\frac{1}{\tau_B^{VT}\alpha}+\frac{K_A}{\tau_A^{VT}\alpha}\exp\left(-\frac{\theta_A-\theta_B}{T}\right)\right]-\\-\varepsilon_B\frac{\alpha-1}{\alpha}\frac{\theta_A-\theta_B}{T}\frac{dT}{dt}+\frac{\varepsilon_C-\varepsilon_B\exp(-(\theta_A-\theta_B)/T)}{\alpha}+(D-\varepsilon_B)\frac{1}{N_B}\left(\frac{dN_B}{dt}\right)_C\\K_A=\frac{N_A}{N_B},\qquad\alpha=1+K_A\exp\left(-\frac{\theta_A-\theta_B}{T}\right)\end{gathered} \tag{6}$$

The relaxation time of the mixture of oscillators A and B is a function of the composition, the pressure, and the transition probability, which, in its turn, depends on the molecular parameters and the temperature. The probabilities of V−V and V−T transitions is calculated according to the SSH theory [9]. In the derivation of a formula for the reaction time [10] the quasistationarity condition is assumed for all low-frequency oscillators of $N_2O$. In the calculation of the flow in the nozzle the temperature of the symmetric and the deformation vibrations is assumed to be equal to the gas temperature.

Under conditions of intense vibrational nonequilibrium the following dissociation mechanism is assumed. Vibrationally excited molecules of $N_2$ efficiently pump the antisymmetric type of vibrations of $N_2O$ and the dissociation of the $N_2O$ molecules takes place by means of the process of predissociation, that is, by a transition of a molecule into the continuous spectrum with a vibrational level lying above the minimal dissociation energy (for $N_2O$ $D_{min}=58$ kcal/mole [7]). In the simplest case the dissociation rate W under nonequilibrium conditions can be represented by the equation [11]

$$\dot{W}=ZN_BP\frac{k}{Q}\beta Q'\exp\left(-\frac{D_{\min}}{RT}\right)\exp\left\{k\theta_B\left(\frac{1}{T}-\frac{1}{T_1}-\frac{\gamma_0}{3D_B}\right)\right\}(1+J_k)^{-1} \tag{7}$$

Here Z is the number of collisions; $T_1$ is the vibrational temperature of the antisymmetric vibration of $N_2O$ at the first level; $\beta$ is a factor that takes account of the contribution of all vibrational levels of the transition probability $i+1 \rightarrow i$; Q' is the probability of a resonance exchange within the limits of an antisymmetric vibration; the parameter $T_k$ determines deviations from the quasiequilibrium dissociation threshold; $\gamma_0 = 0.32\,\alpha^{-1}\sqrt{\mu/TE_1}$; $\alpha$ is the characteristic parameter in the exponential potential $e^{-\alpha r}$; $\mu$ is the reduced collision mass; $D_B$ is the dissociation limit for a B vibration (antisymmetric vibration); and P is the probability of a nonadiabatic transition. The level number k is determined by the relation

$$E_k = k\,[E_1 - (k-1)\Delta E] \leqslant D_{\min} \leqslant E_{k+1} = (k+1)[E_1 - k\Delta E]$$

In its simplest form the kinetics of the dissociation of $N_2O$ is represented by the following scheme:

$$N_2O + M \xrightarrow{1} N_2 + O + M$$
$$O + N_2O \xrightarrow{2} N_2 + O_2$$

We consider the effect of the second reaction in two limiting cases:

1) the rate of reaction (2) is fairly high and supports quasistationarity with respect to 0 atoms, i.e.,

$$d\,[N_2O]/dt = -2k_1\,[N_2O]\,[M]$$

2) the cooling "freezes" reaction (2) and its rate is negligibly small. The first case can be realized only if practically all the activation energy of reaction (2) is surmounted by the vibrational energy of the $N_2O$.

Equation (6) together with the energy equation and the kinetic equation were solved numerically by computer. For the condition on quasistationarity with respect to reaction (2) we applied $\varepsilon_C = D/2$ (such a magnitude can be obtained on the basis of results of [10]). Results of the calculations for this case are represented in Figs. 1a and 1b (Fig. 1a: a mixture 95% $N_2$+5% $N_2O$, T=1500°K, P=10 atm, $\tau_{1/2}$ is the half-conversion time (1); $\tau_r$ is the relaxation time of antisymmetric vibrations of $N_2O$ for V−V equilibrium with vibrations of $N_2$ (2); $\tau_T = T(dT/dt)^{-1}$ is the characteristic cooling time (3); $T_B$ is the vibrational temperature of the antisymmetric vibrations of $N_2O$ (4); and T is the temperature of the gas (5); Fig. 1b: $T_0$=1000°K, $P_0$=1 atm, and the remaining notation is as in Fig. 1a).

It is seen that after x > 5 cm the characteristic half-conversion time $\tau_{1/2}$ becomes less than $\tau^{VT}$ and the magnitude of $\tau_{1/2}$ is such that within the limits of the expansion part of the nozzle there is observed a considerable dissociation of $N_2O$, a distribution of densities of $N_2$ (1), $N_2O$ (1), $N_2O$ (2), and of the percentage content of $N_2O$ (3), represented in Fig. 2, T = 1500°K, $P_0$ = 10 atm. Moreover, during subsequent flow in a channel of constant cross section the dissociation rate exceeds the reaction rate and $N_2O$ molecules will continue to dissociate. The resulting degree of dissociation will depend on the relation of rates of dissociation and translational heating because of the chemical reactian and the V−T relaxation.

Figure 3 shows calculations with the second reaction left out of account for $T_0$=1500°K, $P_0$=10 atm, the remaining notation being the same as in Fig. 1. Qualitatively the character of the process is the same as in the previous case, the quantitative differences being mainly in the dissociation rate $T_B$ and the shape of the $\tau_r$ curve (the nonmonotonicity of $\tau_r$ in Fig. 1 is due to energy release).

Results of a calculation for the initial conditions $P_0$=1 atm, $T_0$=1000°K (Fig. 1b), which lie below the thermal explosion threshold of $N_2O$, are of interest. The calculation shows that expansion of the mixture in the nozzle results in dissociation of $N_2O$ and in this case a fundamentally new type of transition of the critical explosion limit is realized.

We consider the reaction

$$N_2O + CO \rightarrow N_2 + CO_2$$

We assume that the reaction rate is determined by the population of molecules at vibrational levels whose overall energy exceeds the activation energy E=23 kcal/mole [7]

$$W = ZP \sum_{n=0}^{n^*} N_n \sum_{m}^{m^*} N_m$$

where $N_n$ and $N_m$ are the populations at the levels m and n, determined from the Treanor distribution (see (2)). At the same time $E_n + E_m \geq E$, $P = 10^{-3}$ being the steric factor. The calculations show that during expansion of the mixture $N_2O$+CO in a nozzle conditions can be produced for which $\tau_c < \tau_{VT}$, that is, an exchange reaction is realized in a time that is less than the relaxation time. If energy release occurs principally in vibrational stages of $N_2$ and CO, this will result in a further acceleration of the reaction. The fact that the reaction products generally have a longer relaxation time than the original reagents also favors the maintenance of nonequilibrium.

Despite the approximate character of the calculation (mainly because of the lack of a sufficiently reliable theory of dissociation under nonequilibrium conditions), it is assumed that one can look forward to the experimental observation of dissociation during cooling in a supersonic expanding stream. Moreover, the possibility of realizing volumetric reactions ($N_2O+CO$, $HI+F_2$, and others) in a time that is less than the V−T relaxation time is of great interest.

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