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POSSIBILITY OF DISSOCIATION REACTIONS
OCCURRING IN POLYATOMIC MOLECULES
DURING RAPID COOLING IN AN EXPANDING
SUPERSONIC FLOW

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Foreign Technology Division
Wright-Patterson Air Force Base, Ohio

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Block	Italic	Transliteration	Block	Italic	Transliteration
А а	<i>А а</i>	A, a	Р р	<i>Р р</i>	R, r
Б б	<i>Б б</i>	B, b	С с	<i>С с</i>	S, s
В в	<i>В в</i>	V, v	Т т	<i>Т т</i>	T, t
Г г	<i>Г г</i>	G, g	У у	<i>У у</i>	U, u
Д д	<i>Д д</i>	D, d	Ф ф	<i>Ф ф</i>	F, f
Е е	<i>Е е</i>	Ye, ye; E, e*	Х х	<i>Х х</i>	Kh, kh
Ж ж	<i>Ж ж</i>	Zh, zh	Ц ц	<i>Ц ц</i>	Ts, ts
З з	<i>З з</i>	Z, z	Ч ч	<i>Ч ч</i>	Ch, ch
И и	<i>И и</i>	I, i	Ш ш	<i>Ш ш</i>	Sh, sh
Й й	<i>Й й</i>	Y, y	Щ щ	<i>Щ щ</i>	Shch, shch
К к	<i>К к</i>	K, k	Ъ ъ	<i>Ъ ъ</i>	"
Л л	<i>Л л</i>	L, l	Ы ы	<i>Ы ы</i>	Y, y
М м	<i>М м</i>	M, m	Ь ь	<i>Ь ь</i>	'
Н н	<i>Н н</i>	N, n	Э э	<i>Э э</i>	E, e
О о	<i>О о</i>	O, o	Ю ю	<i>Ю ю</i>	Yu, yu
П п	<i>П п</i>	P, p	Я я	<i>Я я</i>	Ya, ya

* ye initially, after vowels, and after ъ, ь; e elsewhere.
 When written as ѣ in Russian, transliterate as yě or ě.
 The use of diacritical marks is preferred, but such marks may be omitted when expediency dictates.

POSSIBILITY OF DISSOCIATION REACTIONS
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Yu. V. Chirikov
(Moscow)

Studied is the possibility of the occurrence of the dissociation reaction of N_2O and the exchange reaction of $N_2O + CO \rightarrow N_2 + CO_2$ in rapid cooling of a gas mixture as a result of supersonic expansion in a nozzle. Balance equation for vibrational energy and the kinetics of the chemical reaction under nonequilibrium conditions are solved numerically. The values of parameters necessary for experimental observations of the studied phenomenon are found.

The rapid exchange of vibrational quantum usually leads to the establishment of quasi-equilibrium vibrational distributions existing in such a course of time t that $\tau^{VV} < t < \tau^{VT}$, where τ^{VV} and τ^{VT} represent the times of V-V and V-T processes, respectively

For example, in a system of oscillators A and B when V-V equilibrium is reached, the following relationship between temperatures T_A and T_B is established [1, 2]

$$\theta_B/T_B = \theta_A/T_A - (\theta_B - \theta_A)/T \quad (1)$$

where θ_A and θ_B are the characteristic temperatures of oscillators A and B, respectively, T - gas temperature.

Under certain conditions ($\theta_B > \theta_A$, $T_A, T_B \gg T$) there may occur a significant vibration pumping of oscillators with a lower quantum energy from oscillators with a higher quantum energy. In a system of anharmonic oscillators under nonequilibrium conditions the pumping of energy to higher levels may lead to a significant increase in the "temperature" of these levels. The population distribution with respect to the levels of an anharmonic oscillator (generally the term "Trinor distribution" is used) is described by the equation [3, 4]

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

Here N_n is the concentration of particles at level n, Q - the statistical sum of the anharmonic oscillator and its anharmonicity ($^{\circ}\text{K}$), respectively, T_1 - effective vibration temperature for levels 1-0. Since the rates of many chemical reactions are determined by the population of rather high vibrational levels, it is interesting to examine the effect of energy pumping under nonequilibrium conditions on the occurrence of certain model reactions. The dissociation and exchange reactions are convenient in this case. The constant of the dissociation rate is determined by the degree of vibrational excitation of the dissociating molecules. The dependence between the rate of the exchange reactions and vibrational excitation of the original reagent has apparently not been sufficiently studied, although the series of studies of Bauer and co-authors (see, for example, [5]) definitely showed that vibrational excitation played a deciding role in a great number of exchange reactions. The experiments in HI and DI molecular beams showed [6] that these molecules, even at a very high translational energy (from 20 to 109 Cal/mole in a mass center system, i.e., high

activation energies) do not enter into the exchange reaction where HD is formed unless they possess sufficient vibrational energy.

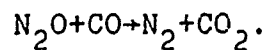
Thus, if we are limited to merely the gas dynamic methods of cooling (for example, the flow in a nozzle), then the factors which cause the reactions to occur at low temperatures are as follows:

1) nonresonance vibrational pumping of "working" molecules from inert biatomic molecules with great relaxation time (for example, N_2);

2) increasing population of high levels of working molecules through anharmonicity (see equation (2)). The considerable decline in density in the case of a flow in a nozzle brings about a corresponding decrease in the delay of the chemical reaction.

Under conditions of a break between the vibrational temperature and the translational the population of the rather high vibrational levels when distribution (2) can be made may increase when the translational temperature decreases. As a result one might expect a corresponding increase in the velocity of certain dissociation and exchange reaction as the temperature declines.

We have selected as our subject of study the decay of N_2O and the exchange reaction



The following factors are responsible for the selection of these systems:

1) The main contributor to the relaxation rate should be level n , for which V-T-relaxation is not yet substantial (i.e., $n < n^*$, where n^* is the level at which the rates of V-V and V-T-processes are compared). Thus, of the dissociation processes the

most similar appeared to be nonadiabatic reactions with predissociation.

2) The activation energy of the reaction $N_2O + CO$ according to the data of [7] equals 23 Cal/mole, i.e., for vibrational levels with such energy $n < n^*$.

3) In molecules with more than 3 atoms it is difficult to separate the vibration temperature from the translational because of the great rate of the intramolecular V-V exchange.

4) Both of the selected reactions are exothermal, and we can thus expect an acceleration of the reaction due to the vibrational energy which is released.

The purpose of the given study was to establish the possibility of experimentally observing decomposition and exchange reactions under flow conditions in nozzles used in connection with shock tubes.

Let us study a flow of a mixture of 5% $N_2O + 95\% N_2$ through a plane nozzle (height, d in critical section 1 mm, length 20 cm, divergence angle $\alpha \approx 12^\circ$). To find the main characteristics of the flow it is sufficient to limit ourselves to approximate analytical relationships

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

which express gas temperature and density in terms of the Mach number (M), the ratio of heat capacity, and the initial parameters T_0 and ρ_0 at the nozzle input. In mixtures with a low concentration of a reacting additive this approximation is quite satisfactory. The dependence of the Mach number along the nozzle is determined from the solution to the equation

$$\left(\frac{F}{F_0}\right)^2 = \frac{1}{M^2} \left[\frac{2}{\gamma-1} \left(1 + \frac{\gamma-1}{2} M^2 \right) \right]^{(\gamma+1)/(\gamma-1)}$$

where (F/F_0) is the ratio of the current area of the cross section to the area in the critical section.

Let us write the equation for the rate of change in the number of vibrational quanta falling within the antisymmetrical vibration of $N_2O(\epsilon_B)$ and the vibration of nitrogen (ϵ_A) [4, 8]

$$\frac{d\epsilon_A}{dt} = -\frac{\epsilon_A - \epsilon_A^0}{\tau_A^{VT}} - Q_{10}^{01} N_B \left[\epsilon_A (\epsilon_B + 1) \exp\left(\frac{\theta_A - \theta_B}{T}\right) - \epsilon_B (\epsilon_A + 1) \right] + (\epsilon_C - \epsilon_B) \frac{1}{N_A} \left(\frac{dN_A}{dt} \right)_C \quad (4)$$

$$\frac{d\epsilon_B}{dt} = -\frac{\epsilon_B - \epsilon_B^0}{\tau_B^{VT}} + Q_{10}^{01} N_A \left[\epsilon_A (\epsilon_B + 1) \exp\left(\frac{\theta_A - \theta_B}{T}\right) - \epsilon_B (\epsilon_A + 1) \right] + (D - \epsilon_B) \frac{1}{N_B} \left(\frac{dN_B}{dt} \right)_C \quad (5)$$

Here ϵ_A^0 and ϵ_B^0 are the equilibrium values of the numbers of vibrational quanta per one molecule; τ_A^{VT} and τ_B^{VT} are the times of vibrational-translational relaxation of molecules A and B; N_A and N_B - the densities of the molecules; θ_A and θ_B - characteristic temperatures; D - dissociation energy; θ_{10}^{01} - probability of vibrational quanta exchange between molecules A and B; ϵ_C - number of vibrational quanta per one molecule A arising in the exothermal reaction.

If we use the model representing rapid vibrational quanta exchange [1, 8], then we get an equation for ϵ_B under the condition $\epsilon_B \ll 1$ taking into account variable gas temperature, the chemical activation A molecule, and the dissociation of B molecules

$$\frac{d\epsilon_B}{dt} = -(\epsilon_B^0 - \epsilon_B^0) \left[\frac{1}{\tau_B^{VT}} + \frac{K_A}{\tau_A^{VT}} \exp\left(-\frac{\theta_A - \theta_B}{T}\right) \right] - \epsilon_B \frac{\alpha - 1}{\alpha} \frac{\theta_A - \theta_B}{T} \frac{dT}{dt} + \frac{\epsilon_C - \epsilon_B \exp\left(-(\theta_A - \theta_B)/T\right)}{\alpha} + (D - \epsilon_B) \frac{1}{N_B} \left(\frac{dN_B}{dt} \right)_C$$

$$K_A = \frac{N_A}{N_B}, \quad \alpha = 1 + K_A \exp\left(-\frac{\theta_A - \theta_B}{T}\right) \quad (6)$$

The relaxation time of the mixture of oscillators A and B is a function of composition, pressure, and the probabilities of transfer, which in turn depend on the molecular parameters and temperature. The probability of V-V and V-T transitions are calculated according to the SSH theory of [9]: in deriving the formula for relaxation time [10] the condition of quasi-stationarity was assumed for all low-frequency N_2O oscillators. In calculating the flow in the nozzle the temperatures of symmetrical and deformed vibrations were assumed to be equal to the gas temperature.

Under conditions of an intense vibrational imbalance the following dissociation mechanism is used. Vibration excited N_2 molecules effectively pump the antisymmetrical type of N_2O vibrations, and the decomposition of a N_2O molecules occurs by predissociation, i.e., during the transition of the molecule into the continuous spectrum from the vibrational level which is above the minimal dissociation energy (for N_2O $D_{\min} = 58$ Cal/mole [7]). In the simplest case the dissociation rate (W) under nonequilibrium conditions can be represented by the equation [11]

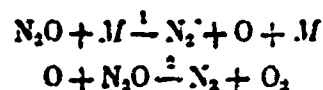
$$W = Z N_B P \frac{k}{Q} \beta Q' \exp\left(-\frac{D_{\min}}{RT}\right) \exp\left\{\lambda D_B \left(\frac{1}{T} - \frac{1}{T_1} - \frac{\gamma_0}{3D_B}\right)\right\} (1 + J_0)^{-1} \quad (7)$$

Here Z is the number of collisions, T_1 - the vibrational temperature of the antisymmetrical N_2O vibration on the first level, β - the factor which considers the participation of all vibrational levels in the probability of transition $i+1 \rightarrow i$; Q' - probability of resonance exchange within limits of antisymmetrical vibration, parameter T_H determines deviations from quasi-equilibrium at dissociation boundary; $\gamma_0 = 0.32 \alpha^{-1} \sqrt{\mu / T E_1}$; α - characteristic parameter in exponential potential $e^{-\alpha r}$; μ - reduced mass of collision; D_B - dissociation limit for B vibration (antisymmetrical vibration); P - probability of nonadiabatic transition. The

number of the level k is determined by the relationship

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

The decay kinetics of N_2O in their simplest form are represented by the following scheme:



We will examine the effect of the secondary reaction in the two limiting cases:

1) The rate of the reaction (2) is sufficiently great, and quasi-stationarity is maintained with respect to the concentration of O atoms, i.e.,

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

2) Cooling "freezes" the reaction of (2) and its rate is negligible small. The first case can be realized only if almost all of the activation energy of reaction (2) is overcome by the vibrational energy N_2O .

A numerical solution on the electronic computer was found jointly for equation (6), the equation of energy, and the kinetic equation. Under the condition of quasi-stationarity with respect to the reaction (2) we assume $\epsilon_c = D/2$ (this value can be obtained on the basis of the results of [10]). The results of calculations for this case are shown in Figs. 1a and 1b (Fig. 1a - mixture of 95% N_2 + 5% N_2O , $T=1500^\circ K$, $P=10$ atm, $\tau_{1/2}$ - time of half-conversion (1); τ_r - relaxation time of antisymmetrical N_2O vibrations under V-V-equilibrium with N_2 vibrations (2); $\tau_T = T(dT/dt)^{-1}$ - characteristics cooling time (3); T_B - vibrational temperature of antisymmetrical N_2O vibrations (4); T - gas temperature (5); Fig. 1b -

$T_0=1000^\circ\text{K}$, $P_0=1\text{ atm}$, remaining symbols as in Fig. 1a).

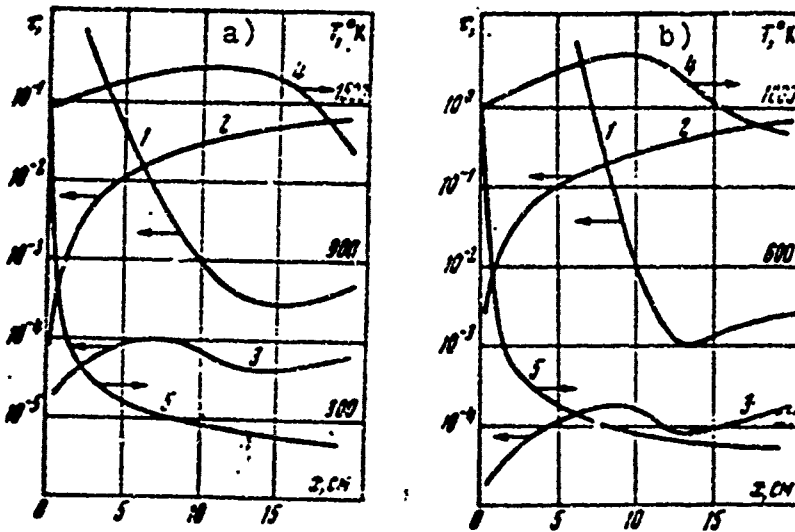


Figure 1a, b

We see that after $x > 5$ cm the characteristic half-conversion time $t_{1/2}$ becomes less than τ^{VT} , while the value of $\tau_{1/2}$ is such that we already observe a noticeable decomposition in N_2O within the limits of the expanding part of the nozzle. The distributions for the densities of N_2 (1), N_2O (1), and N_2O (2) and the percent concentration of N_2O (3) are shown in Fig. 2; $T=1500^\circ\text{K}$, and $P_0=10\text{ atm}$. Moreover, as the flow continues in a channel with a constant cross section the rate of decay exceeds the relaxation rate, and the N_2O molecules continue to decompose. The resulting degree of expansion will depend on the relationship of the rate of decay and translational heating caused by the chemical reaction and V-T relaxation.

Figure 3 shows calculations which do not consider the secondary

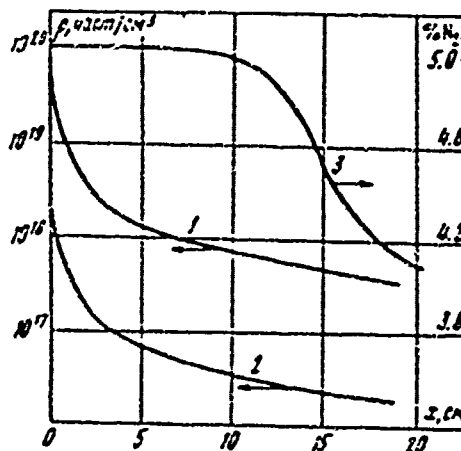


Figure 2

reactions for $T_0=1500^\circ\text{K}$, $P_0=10$ atm, and the remaining symbols as in Fig. 1. Qualitatively the nature of the process is the same as the preceding case, and the quantitative differences belong primarily to the rate of the drop in the T_B and the form of the τ_T (the nonmonotonic nature of τ_T on Fig. 1 is caused by the energy release).

Interesting are the results of calculating for initial conditions $P_0=1$ atm, $T_0=2000^\circ\text{K}$ (Fig. 1b) the line below the thermal explosion limit for N_2O . The calculation shows that expansion of the mixture in the nozzle leads to an expansion of N_2O even when the theoretically new transition of the critical explosion limit is realized.

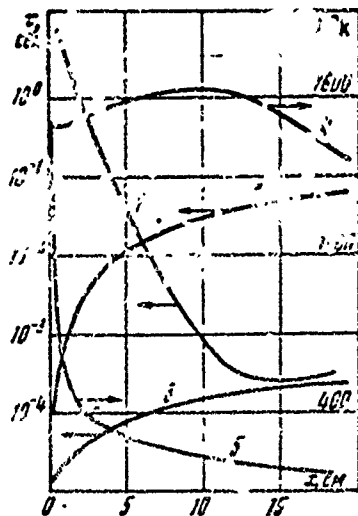
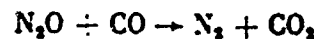


Figure 3

Let us look at the reaction



We will assume that the reaction rate is determined by the molecule population on the vibrational levels whose sum energy exceeds activation energy $E=23$ Cal/mole [7]

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

where N_n and N_m are the populations on levels m and n , determined from the Trivior distribution (see (20)). Here $E_n + E_m > E$, $P=10^{-3}$ is the steric factor. The calculations show that when the mixture of $\text{N}_2\text{O}+\text{CO}$ expands in a nozzle conditions may be created under which $\tau_c < \tau_{VT}$, i.e., an exchange reaction may occur during times smaller than the relaxation time. If the release of energy occurs primarily in vibrational degrees of freedom of N_2 and CO , then this will lead

to a further acceleration in the reaction. Also advantageous from the standpoint of maintaining equilibrium is the fact that the reaction products have, generally speaking, greater relaxation times than the original reagents.

Despite the approximate nature of the calculation (resulting primarily from the fact that there does not exist a sufficiently reliable dissociation theory under nonequilibrium conditions), we believe that the experimental observation of the decomposition during cooling in a supersonic expanding flow is reliable. Moreover, the possibility of exchange reactions (N_2O+CO , $HI+F_2$, and others) occurring during times less than the V-T relaxation times is extremely interesting.

31 January 1972

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