The physics of a chemically active plasma with nonequilibrium vibrational excitation of molecules

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The results of experimental and theoretical studies of chemical reactions in nonequilibrium plasmas are reviewed. Special attention is given to processes stimulated by vibrational excitation of the ground electronic state of the reacting molecules in the plasma. General patterns in the kinetics of these reactions are discussed, and the optimum discharge parameters for maximum energy efficiency are noted. Specific plasma-chemical processes—the dissociation of CO_2 and H_2O and the synthesis of nitrogen oxides—are described. Experimental results are presented for hf, microwave, glow, plasma-beam, and non-self-sustained discharges, for plasma radiolysis, etc.

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INTRODUCTION

The nonequilibrium electrical discharge in gases occupies an important position among the many and varied nonequilibrium systems that have been studied intensively during recent decades. In the gas discharge, electric-field energy is transferred to the electrons of a weakly ionized plasma, which, in turn, maintain above-thermal population of the excited atomic and molecular states. Neutral particles excited by electrons can transfer their energy to coherent radiation, as occurs in gas lasers, and can also stimulate selective atomic-molecular conversions, such as those brought about in nonequilibrium plasma-chemical systems. The chemically active plasma with which this review is concerned has attracted the atlention of investigators as a system that makes it possible to conduct selective chemical reactions at extremely high rates. Variation of the plasma's parameters makes it possible to control the chemical processes, direct them into the desired channel, and optimize their energy efficiency. The present review is devoted to the physical kinetics of the chemically active plasma and primarily to the kinetics of nonequilibrium processes stimulated by vibrational excitation of molecules in the gas-discharge plasma.

Until recently, studies of nonequilibrium plasmachemical processes were made for the most part in reduced-pressure glow discharges. Considerable pro-

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gress was made here in polymerization, treatment of surfaces with low-temperature plasmas (physical pickling), and investigation of the mechanisms of nonequilibrium processes.¹ In recent years, largely as a result of the development of gas-laser physics, the range of discharge systems that can be used in nonequilibrium plasma chemistry has been broadened significantly. Nonequilibrium chemical processes are now being investigated successfully in non-self-sustained discharges sustained by ultraviolet radiation or by relativistic-electron beams, in hf and microwave discharges (Table I), and in fast-flow glow discharges at elevated pressure. The low-pressure plasma-beam discharge, which uses collective processes to heat plasma electrons, was developed specifically for plasma-chemical applications.¹⁵⁹

The mechanisms by which chemical reactions are brought about under nonequilibrium conditions are distinguished by their wide variety. Depending on the degree of ionization, electron temperature, pressure, and the specific energy intensity of the discharge, a given resultant process may be brought about in fundamentally different ways with widely differing energy efficiencies. D. I. Slovetskii *et al.*^{1,7} made a detailed investigation of the mechanisms of several nonequilibrium plasma-chemical processes for the case of the glow discharge. Among other things, they determined the principal reactions that determine the dissociation of nitrogen, ammonia, and carbon dioxide in the glow discharge.

Research in the physics of gas lasers and laser chemistry drew attention to the importance of vibrational excitation of molecules in the organization of nonequilibrium processes and selective reactions. For most nonelectronegative molecules (N₂, CO, CO₂, H₂, H₂O, etc.), vibrational excitation by electron impact occurs not in a process of direct collision (which is inefficient owing to the small electron-to-molecule mass ratio), but via the formation of an intermediate autoionization state.²²⁻²⁴ As a result, the rate of vibrational excitation of these molecules is quite high (Table II), and most of the discharge energy input is localized precisely on the vibrational degrees of freedom, which can ensure selectivity and, consequently, high energy efficiency of the processes. Vibrational disequilibrium $(T_v > T_0)$ is maintained here by the low rate of VT re-

TABLE I. Maximum energy efficiencies of plasma-chemical processes.

	Equilibrium regime			Nonequilibrium regime		
Process	Calcu- lated, %	Experi- mental, %	Type of dis- charge	Calcu- lated, %	Experi- mental, %	Type of dis- charge
$CO_z \rightarrow CO + \frac{1}{2}O_z - 2.9 \text{ eV}$	43	15	Electric- arc	80	80	Microwave
$\frac{1}{2}N_2 + \frac{1}{2}O_2 \rightarrow NO - 1 \text{ eV}$	11	2—3	Same	45	3 0	Pulsed microwave with mag- netic field
$H_2O \rightarrow H_2 + \frac{1}{2}O_2 - 2.6 \text{ eV}$	-	-	_	5 0—70	40	Microwave

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TABLE II. Rate constants of vibrational excitation by electron impact, $\rm cm^3/sec$.

	Electron temperature				
Molecule	0.5 eV	1 eV	2 eV		
Hydrogen	2.2.10-10	2.5.10-10	0.7.10-		
Nitrogen	2.10-11	4.10-9	3.10-8		
Deuterium	-	-	10-9		
Carbon dioxide	3.10-9	10-8	3-10-8		
Carbon monoxide	-	- 1	10-7		
Water vapor	-	- 1	10-10		
Oxygen		-	16-9-10-1		

laxation at the low translational temperature T_0 (see Table IV below). For nonequilibrium plasma chemistry, the mechanism of vibrational molecular excitation by electron impact is characterized by an important specific advantage: it is this mechanism that is capable of stimulating chemical conversions with the highest energy efficiency as compared to the other plasma-chemical reaction channels. This is an effect of the following three basic causes:

1. For many nonelectronegative-gas molecules at electron temperatures $T_e = 1-3$ eV, a major part of the discharge energy input is concentrated precisely on excitation of vibrational degrees of freedom of the ground electron states. This effect is illustrated graphically in Figs. 5, 16, and 24 for the CO₂, N₂, and H₂O molecules.

2. It is the vibrational energy of the reagents that is most effective in overcoming the activation barriers of endoergic reactions,⁸ the realization of which in the nonequilibrium plasma is of the greatest interest. This effect has been confirmed experimentally, for example, by the kinetics of laser-chemical reactions,⁹ by reactions with energy branching,¹⁰ and by study of the energy distribution of the products of the excergic reverse reactions.¹¹ It is clearly illustrated by Table III.

3. In the vibrational excitation of molecules, the energy threshold usually coincides with the activation barrier of the reaction and is found to be quite far below the threshold of the reaction via electronic excitation of the reagents. Thus, the vibrational excitation

TABLE III. Efficiency of vibrational-energy utilization in overcoming elementary-reaction energy thresholds.

Reaction	ΔH, eV	E _a , eV	a
1. $S+CO \rightarrow CS+O$ 2. $O+N_2 \rightarrow NO+N$ (nonadiabatic	3.6 3.2	3.7 3.2	0.9-1.0
$\begin{array}{c} (channel) \\ channel) \\ 3. J + HCI \rightarrow HJ + CI \\ 4. H + HF \rightarrow H_{3} + F \\ 5. OH^{\bullet} + O_{3} \rightarrow OH + O_{2} + O \\ 6. OH^{\bullet} + O_{3} \rightarrow 2O_{2} + H \\ 7. O_{3}^{\bullet} + O_{4} + (1A_{2}) \rightarrow 2O_{2} + O \\ 8. O + H_{2} \rightarrow OH + H \\ 9. O + HCI \rightarrow OH + CI \\ 10. H + H_{3} \rightarrow H_{3} + H \\ 11. H + HCI \rightarrow HCI + H \\ 12. H + HCI \rightarrow HCI + H \\ 12. H + HCI \rightarrow H_{2} + CI \\ 13. O_{3}^{\bullet} + NO \rightarrow NO_{2} (^{\circ}B_{2}) + O_{2} \\ 14. O_{3}^{\bullet} + NO \rightarrow NO_{2} (^{\circ}B_{3}) + O_{2} \\ 15. O_{4}^{\bullet} + SO \rightarrow SO_{3} (^{\circ}B_{3}) + O_{2} \\ 16. O^{\bullet} + N_{2} \rightarrow NO^{\bullet} \rightarrow N \\ 17. N + O_{3} \rightarrow NO_{4} (^{\circ}B_{3}) + O_{2} \\ 18. F + HCI \rightarrow HF + CI \\ 19. OH^{\bullet} + O_{3} \rightarrow HO_{2} + O_{4} \\ 20. O_{3}^{\bullet} + NO \rightarrow NO_{3} (^{\circ}A_{3}) + O_{2} \\ 21. H + N_{2} O \rightarrow N_{2} + OH \end{array}$	$\begin{array}{c} 1.4\\ 1.4\\ 1.4\\ 1.1\\ 0.3\\ 0.1\\ 0.05\\ 0.02\\ 0\\ 0\\ -0.05\\ -0.3\\ -0.9\\ -1.1\\ -1.2\\ -1.4\\ -1.4\\ -1.5\\ -2.1\\ -2.7\end{array}$	$\begin{array}{c} - \\ 1.5 \\ - \\ 0.4 \\ 0.2 \\ 0.3 \\ 0.2 \\ 0.2 \\ 0.2 \\ 0.2 \\ 0.2 \\ 0.5 \\ 0.05 \\ 0.1 \\ 0.5 \end{array}$	$\begin{array}{c} 1,0-1,1\\ 1,0-1,1\\ 0,02\\ 0,02\\ 1\\ 0,3-0,4\\ 0,3\\ 0,3\\ 0,3\\ 0,3\\ 0,3\\ 0,3\\ 0,3\\ 0,3$

of hydrogen requires 4.4 eV (the bonding energy) for dissociation, while dissociation of hydrogen by electron impact via the ${}^{3}\Sigma_{u}^{*}$ state requires at least 8.8 eV. In the case of CO₂, the energy of the O-CO bond is 5.5 eV, while electron-impact dissociation via the ${}^{1}B_{2}$ and ${}^{3}B_{2}$ states requires ~8 eV per event. The effect is seen clearly in Fig. 8, where the lower electronic terms of CO₂ are represented with allowance for the geometric nonlinearity of the excited states.¹²

Under the most favorable conditions, vibrational excitation of reagents in a plasma makes it possible to concentrate up to 80% of all of the energy introduced into the discharge on accomplishment of the chemical processes.¹³ This energy efficiency cannot be obtained in other plasma-chemical reaction channels. In reactions proceeding via electronically excited states (see Figs. 3 and 4), for example, none of the three effects listed above comes about, with the result that high efficiencies are not attained.^{14,15} For example, an efficiency $\eta < 30\%$ is obtained in the dissociation of CO₂ by this mechanism.¹⁶ Lowering of the electron threshold energy to the bonding energy is possible on electronic excitation of previously vibrationally pumped molecules,^{1,14} but localization of the bulk of the energy input in this channel, especially with dissociation, is improbable.^{1,13,14} The attainment of high energy efficiency is also made difficult in another alternative mechanismdissociative sticking (see Figs. 4 and 19).¹⁷⁻¹⁹ Here the efficiency is limited primarily by the loss of the electron in the sticking event.¹⁾ The efficiency in this case is lowered by the high "energy cost" of producing one electron in the discharge (\geq 30 eV), which is considerably higher than the energy expenditure needed per dissociation event.²⁷²⁰

While we are on the subject of chemical reactions in gas discharges, we must also mention quasiequilibrium plasma chemistry—a traditional approach that has been developed by a large group of investigators.¹⁻⁵ The arc plasmatrons with powers up to 10 MW and the hf plasmatrons of somewhat lower power that have been developed in recent decades have made it possible to use quasi-equilibrium plasma to solve a number of important scientific and practical problems, of special importance among which are the production of acetylene from methane, the synthesis of refractory compounds, coal conversion, and the processing of titanium compounds.¹ However, the high nonadiabatic product cooling rates required in these systems (see Fig. 2) and the uniformity of the energy input over all degrees of freedom mean that the quasiequilibrium plasmatron offers practically no promise for the conduct of selective chemical reactions with high energy efficiency. The energy advantages of nonequilibrium systems are clearly illustrated in Table I for various specific processes.³⁾

Thus, a nonequilibrium plasma-chemical process stimulated by vibrational excitation of molecules on electron impact can guarantee maximum energy efficiency.⁴⁾ However, attainment of regimes with maximum energy efficiency depends strongly on the parameters of the discharge; at low energy inputs and low degrees of ionization, for example, reactions of vibrationally excited molecules hardly proceed at all, and, conversely, overheating effects and disruption of the nonequilibrium state may occur at excessively high energy inputs. Determination of the energetically optimal regimes requires both experimental and theoretical study of the mechanisms and vibrational kinetics of specific plasma-chemical processes. This paper will review studies of this kind as they apply to moderatepressure systems exemplified by certain inorganicsynthesis and dissociation reactions under nonequilibrium-plasma conditions. The first part of the review is devoted to analysis of the general laws governing plasma-chemical reactions stimulated by vibrational excitation of molecules. Specific plasma-chemical processes are examined under subsequent headings. For example, processes of decomposition of CO₂ and H₂O, which, apart from their scientific importance, are of great practical interest in applied atomic-hydrogen power engineering, are discussed in Secs. 2 and 3 as examples of dissociation in plasma. The process of atmospheric-nitrogen binding in plasma is discussed in Sec. 4 of the review as an example of a plasma-chemical synthesis reaction. In describing specific plasmachemical processes stimulated by vibrational excitation of molecules, attention is concentrated on the theoretical background and experimental illustrations of the possibility of setting up processes in which a major part of the energy injected into a plasma is converted into system chemical energy.

1. VIBRATIONAL KINETICS AND REACTIONS OF VIBRATIONALLY EXCITED MOLECULES IN A NONEQUILIBRIUM PLASMA

To describe specific plasma-chemical processes and to determine optimum conditions for them it is necessary first to analyze general problems in the reaction kinetics of molecules in a nonequilibrium plasma. Plasma-chemical reactions stimulated by vibrational excitation of molecules are characterized by the following basic energy-transformation stages. First, electric-field energy is converted to electron-gas thermal energy, which is then transferred to lower vibrational levels of the ground electron state of the molecules.

¹⁾The possibility of recovering the electron on decomposition of the negative fragment ion will be discussed below in connection with the decomposition of water vapor in plasma.

²⁾Similar effects limit the dissociative-recombination energy efficiency in ion-molecule reactions, reactions in which excited atoms participate, etc.²¹

³⁾Even at quasiequilibrium between the forward and reverse reactions, the transition to systems with $T_{V} > T_0$ (T_V is the vibrational temperature) raises the efficiency as compared to the variant at full equilibrium—in the particular case of the dissociation of CO₂, this efficiency increase may reach 1.5.⁶ On the whole, quasiequilibrium generally does not prevail between forward and reverse reactions in nonequilibrium plasmas.⁷

⁴)We note that vibrational excitation of the ground electron state may not be the optimum from the standpoint of energy efficiency for strongly electronegative and polyatomic molecules.

Then highly excited states of the molecules, those that stimulate chemical conversions in endoergic reactions⁵⁾ (on which we shall concentrate most of our attention in this review), are populated in a process of vibrationalvibrational (V-V) quantum exchange. Accordingly, calculation of the kinetics of these plasma-chemical processes requires, along with analysis of the elementary-reaction cross sections, investigation of the energy distribution functions of both the electrons and the vibrationally excited molecules. In general, this investigation must be of self-consistent nature, which is especially important at high degrees of ionization.58,159 However, since the energy thresholds of vibrational excitation are relatively low, it is unnecessary in some cases to have complete information on the electron energy distribution function $f_{\bullet}(E_{\bullet})$, and the parameters that describe only the initial $f_{\bullet}(E)$ segment are sufficient.

A specific property of elementary atomic-molecular processes in a nonequilibrium plasma is that the translational and rotational energies are much smaller than the vibrational energy of the molecules. This is especially important, since it is the vibrational energy that is most effective in surmounting the energy thresholds of endoergic reactions.^{8,25,47} If, to illustrate, we assume that the vibrational energy E only shifts the reaction activation barrier by an amount $\alpha E(k_{\rm R}(E, T_0))$ $\sim \exp[(\alpha E - E_{\rm s})/T_{\rm 0}])$, the relative importance of molecular-vibration excitation will be determined by the coefficient α , which has come to be known as the vibrational-energy utilization efficiency and is now widely used in interpretation of experimental results.²⁸⁻³⁰ The correlation of the coefficient α with the enthalpy change in the reaction is evident from Table III, and this is an indication that the acceleration of endoergic processes is due precisely to molecular vibrations.

The present status of experimental and theoretical research on the interactions of vibrationally excited molecules with active atoms has been illuminated quite fully in the review by Nikitin *et al.*⁸ Here we note only that the dynamics of the elementary events can still be described reliably only by the classical-trajectory method.³¹ This description encounters difficulties in determining the nature of the potentlal-energy surfaces,^{30,35,57} and, moreover, does not permit effective allowance for the possible nonadiabatic transitions.^{32,33} In some cases, however, it is possible to describe the elementary processes within the framework of simplified, including statistical, models^{34,35}; one of these variants will be considered below as exemplified by the synthesis of nitrogen oxides in a plasma.

The kinetics of these plasma-chemical processes are most significantly influenced by the nature of the vibrational population of highly excited states, which is de-

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TABLE IV. Rate constants of vibrational relaxation of singlecomponent gases ($T_0 = 300$ K).

Molecule	k, cm ³ /sec	Molecule	k, cm ³ /sec	Molecule	k, cm ³ /sec
02 Cl2 Br2 L2 N, CO H2 NO HF DF	$5 \cdot 10^{-16} \\ 3 \cdot 1(i^{-18} \\ 10^{-14} \\ 10^{-18} - 10^{-19} \\ 10^{-18} \\ 10^{-18} \\ 2 \cdot 10^{-13} \\ 5 \cdot 10^{-13} \\ $	HCl DCl HBr DBr HI C ₂ H ₂ N ₂ O COS COS CO ₂	$\begin{array}{c} 3\cdot 10^{-14} \\ 5\cdot 10^{-18} \\ 2\cdot 10^{-18} \\ 10^{-13} \\ 10^{-13} \\ 10^{-13} \\ 10^{-14} \\ 3\cdot 10^{-14} \\ 5\cdot 10^{-14} \\ 5\cdot 10^{-14} \\ 5\cdot 10^{-15} \end{array}$	$\begin{array}{c} H_2O\\SO_2\\CH_2Cl_2\\CH_4Cl_2\\CH_4Cl_3\\CHCl_3\\CCl_4\\D_2\end{array}$	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$

termined by competition between vibrational pumping (eV), VV and VT relaxation processes (Table IV), chemical reactions, and radiation. An extensive literature³⁵⁻⁴⁸ has been devoted to this problem, most of it concerned with description of gas lasers. Here a distinctive aspect of the plasma-chemical problems is detailed allowance for the influence of chemical reactions on the form of the vibrational distribution function. Since this problem has been solved with the greatest clarity for the case of a gas of dlatomic molecules, we shall discuss it in greater detail. Extension of the proposed approach to the case of polyatomic molecules is possible only in the approximation in which vibrational modes are separated³⁷ or, on the other hand, on the assumption that the modes are in equilibrium, with the introduction of vibrational statistical weights.³⁴

Treanor⁴⁸ was the first to propose analytic X(E) representation of the vibrational-level population in VV relaxation with allowance for anharmonicity, but because of divergence in the vibrational energy E this distribution was found to be valid only for relatively low vibrational quantum numbers ($v < (1/2X_e) T_0/T_v$) X_e is the constant of anharmonicity and $T_{\rm V}$ is the vibrational temperature determined using the first few levels. Numerical calculations with further allowance for VT relaxation and radiation were made³⁶⁻³⁹ to determine the populations of the highly excited states. The approximate analytic expressions for X(E) that were found in Refs. 42, 44, and 49 describe only particular cases that are of no significant interest for plasmachemical applications; the approaches proposed are also quite unwieldy and do not permit consideration of the effects of chemical reactions on the vibrational distribution function.

An analytic solution that takes into account the influence of endoergic reactions can be derived within the framework of a diffusion approximation of the molecular fluxes along the vibrational energy spectrum.^{34,38} This approximation is valid if many relaxation-interaction events take place during the characteristic time of variation of the distribution function, a condition that is usually satisfied in a nonequilibrium plasma. The continuity equation in energy space, with VV and VT relaxation processes and reactions, can then be written in the form

$$\frac{\partial^{\prime}}{\partial t} X(E, t) + \frac{\partial}{\partial E} (j_{VV} + j_{VT} - J_R) = 0, \qquad (1.1)$$

where the flux J_{R} determines the loss of excited particles in chemical reactions:

⁵⁾A reaction is considered endo- or excergic if the difference between the ground energy levels of the reagents and the products is negative or positive, respectively. We note that a reaction is regarded as endo- or exothermal in accordance with the sign of the difference between the energies of the levels from which the equilibrium temperature distribution is reckoned.

$$J_{\mathrm{R}}(E) = J_{0} - \int_{0}^{E} k_{\mathrm{R}}(\varepsilon) n_{0} X(\varepsilon) \,\mathrm{d}\varepsilon, \qquad (1.2)$$

 $J_0 = J_{\rm R} (E=0)$ is the total flux of particles into the reaction (if n_0 is the concentration of the molecules, $W = n_0 J_0$ is the over-all rate of the process) and $k_{\rm R}(\varepsilon)$ is the elementary-reaction rate constant, which can be expressed, for example within the framework of the statistical theory of Ref. 34, in terms of the frequency ν_0 of formation of an intermediate complex, the effective number S of its degrees of freedom, and the activation energy E_a in the form

$$k_{\rm R}(E) = \frac{\gamma_0}{n_0} \left(\frac{E - E_{\rm B}}{E}\right)^{S-1}.$$
 (1.3)

In the diffusion equation (1.1), j_{VV} and j_{VT} are the fluxes along the vibrational spectrum due respectively to VV and VT processes. The flux j_{VT} is found in the thermal-reservoir approximation in the form⁵⁰

$$j_{\rm VT} = -D_{\rm VT}(E) \left[\frac{\partial}{\partial E} X(E) + \tilde{\beta}_0 X(E) \right]; \qquad (1.4)$$

here $\hbar \omega$ is the vibrational quantum, the diffusion coefficient is given by $D_{VT}(E) = k_{VT}(E) n_0 (\hbar \omega)^2$ and the temperature parameter $\tilde{\beta}_0$ is defined by the relation $\tilde{\beta}_0 \hbar \omega = 1 - \exp(-\hbar \omega/T_0)$. We note that at high temperatures, $(T_0 \gg \hbar \omega) \tilde{\beta}_0 = T_0^{-1} = \beta_0$, and equating the relaxation flux (1.4) to zero naturally results in a Boltzmann distribution. But as the temperature decreases below the vibrational quantum $\tilde{\beta}_0 < \beta_0 = T_0^{-1}$ which makes the VT relaxation "nonclassical" and weakens the flux (1.4) as compared to the purely classical approximation of the continuous vibrational energy spectrum.⁴⁹

In the general case, the expression for the relaxation flux j_{VV} is rather unwieldy³⁶ owing to the involvement of two vibrationally excited molecules in the VV-exchange process and its consequent strong nonlinearity. At average vibrational energies that are not very high:

$$T_{\rm V} < \hbar\omega \left(\delta_{\rm VV} \hbar\omega + 2X_{\rm e} \frac{T_{\rm V}}{T_{\rm e}} \ln \frac{T_{\rm e} \hbar\omega}{2X_{\rm e} T_{\rm V}^2} \right)^{-1}, \qquad (1.5)$$

which are characteristic for the plasma-chemical systems under study, nonresonant VV exchange with weakly excited molecules prevails, and the expression for $j_{\rm VV}$ can be linearized⁵⁰:

$$j_{VV} = -D_{VV}(E) \left[\frac{\partial}{\partial E} X(E) + \beta_V X(E) - 2\beta_0 X_e \frac{E}{\hbar \omega} X(E) \right]; \quad (1.6)$$

here $\beta_{\rm V} = T_{\rm V}^{-1}$, the diffusion coefficient is $D_{\rm VV}(E) = k_{\rm VV}(E)n_0(\hbar\omega)^2$, and $k_{\rm VV} \sim Ee^{-6}{\rm VV}^E$ is the rate constant of VV relaxation with reservoir molecules ($E \leq T_{\rm V}$). Unlike the flux (1.4), which gives a Boltzmann distribution in the stationary case ($j_{\rm VT} = 0$), the VV flux (1.6) contains a third term that takes into account the overcoming of the anharmonic resonance defect in VV exchange at the expense of translational energy. As a result, we obtain Treanor's distribution⁴⁸ under stationary conditions in the presence of VV exchange alone ($j_{\rm VV} = 0$):

$$X_{\rm T}(E) = B \exp\left(-\beta_{\rm V} E + \beta_0 X_{\rm e} \frac{E^2}{\hbar\omega}\right). \tag{1.7}$$

At high values of the average vibrational energy, when the condition converse to (1.5) is satisfied, VV exchange results in the formation of a plateau on the dis-

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tribution function. In this case, the presence of the resonant terms $|(E_1 - E_2)\delta_{VV}| < 1$ in the general expression for the flux leads to an additional term $\partial(X^2E^2)/\partial E$, which determines the distribution of the vibrational population $X(E) \sim E^{-1} \cdot e^{0.42 \cdot 44 \cdot 51 \cdot 52}$

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The interaction of vibrationally excited molecules with the electron gas is not taken into account explicitly in Eq. (1.1). Actually, it is assumed that the electrons pump only the lower vibrational levels, which determine the reservoir temperature $T_{\rm v}$, which sets a boundary condition for the logarithmic derivative of X(E) and figures later in the form of the parameter $\beta_v = T_v^{-1}$. Here the nature of the distribution function is determined only by the competition of VV and VT relaxation and the reaction. At high degrees of ionization, however, when the frequency of excitation of molecules by electron impact becomes comparable to the frequency of the above relaxation processes, interaction with the electron gas also results in a change in the very nature of the population of the upper vibrational levels.^{38,53-56} The influence of this effect, which includes stepwise vibrational excitation and second-order impacts, is taken into account by introducing an additional flux into the continuity equation $(1.1)^{55}$:

$$\mathbf{f}_{ev} = -D_{ev}(E) \left[\frac{\partial}{\partial E} X(E) + \beta_e X(E) \right], \qquad (1.8)$$

where the diffusion coefficient is given by $D_{ev}(E)$ $=\lambda k_{ev}^{0}(E)n_{0}(\hbar\omega)^{2}, n_{e}$ is the electron concentration, β_{ev} $=T_{e}^{-1}$ is the temperature parameter, $k_{ev}^{0}(E)$ is the rate constant of single-quantum vibrational excitation of molecules with energy E, and the parameter λ determines the contribution of multiquantum eV vibrationalexcitation processes. Unlike VV and VT relaxation, multiquantum eV processes take place with comparatively high probability. Thus, the transfer of Δv quanta is characterized by a small parameter exp($-\alpha \Delta v$). where, for nitrogen molecules as an example, $\alpha = 0.5 - 0.7$.^{53,58} Transfer occurs with the highest probability on excitation of $\Delta v = 2/\alpha$ quanta, and, on the whole, the contribution of multiquantum processes reduces basically to an increase in the effective diffusion coefficient; here the parameter $\lambda \approx 2/\alpha^3$ and, numerically for the nitrogen molecule, $\lambda \approx 10$.

Comparison of the diffusion coefficients $D_{\rm VV}$, $D_{\rm VT}$, and $D_{\rm eV}$ indicates that the influence of eV processes on the form of the distribution function is manifest only at high degrees of ionization,

$$\left(\frac{n_e}{n_0}\right)^2 > \frac{k_{\rm VV}(E=0) k_{\rm VT}(E=0)}{k_{\rm eV}^2 (E=0)}$$
, (1.9)

and results in a gentle exponential decrease of X(E)with an exponent $\beta_{\phi}E$ (practically a plateau). At lower electron concentrations, as we noted, the role of the eV processes reduces to the contribution to the integral vibrational-energy balance alone.

The VV, VT, and eV fluxes discussed above are those of a single-component gas; in the case of a mixture of gases, VV' exchange between various vibrational modes

⁶⁾An analytic solution of the corresponding nonstationary problem (1.1) in the plateau region was given in Ref. 32.

of the system becomes significant. This case has not been considered in as much detail in the literature.^{36,59-61} Intermode VV' exchange results in excitedstate enrichment of components with lower vibrational frequencies (this would be the heavier isotope in the case of an isotope mixture). In the simplest case of a two-component mixture, the VV' flux for the *i*th component can be written in the form⁶²

$$j_{VV'}^{i} = -D_{VV'}^{ij} \left[\frac{\partial}{\partial E} X_{i}(E) - 2X_{e}^{i}\beta_{0} \frac{E}{\hbar\omega_{i}} X_{i}(E) + \beta_{ij}X_{i}(E) \right]; \quad (1.10)$$

here $D_{VV'}^{ij} = k_{VV'}^{ij} (E) n_0 (\hbar \omega_i)^2$, n_j is the concentration of the *j*th component, $k_{VV'}^{ij} (E)$ is the rate constant of VV' relaxation of the *i*th component on molecules of the vibrational reservoir of the *j*th component, the temperature parameter β_{ij} is defined by

$$\beta_{lj} = \frac{\omega_j}{\omega_l T_j} - \frac{\omega_l - \omega_j}{\omega_l T_0}, \qquad (1.11)$$

and T_j is the vibrational temperature of the *j*th component. We note that at mode quasiequilibrium, the relation between the vibrational temperatures of components *i* and *j* can be expressed on the basis of the flux (1.10) in the form of Treanor's formula⁴⁸

$$\frac{\omega_l}{T_i} - \frac{\omega_J}{T_j} = \frac{\omega_l - \omega_J}{T_0} \,. \tag{1.12}$$

We see that the higher the frequency under nonequilibrium conditions $(T_{i,j} > T_0)$, the lower is the vibrational temperature.

The relations obtained for the fluxes j_{VV} , j_{VT} , j_{eV} , and j_{VV} . can be used to solve the problem of the characteristics of the vibrational distribution function with the complete set of relaxation processes being taken into account. Let us consider the simultaneous allowance for VV and VT relaxation in greater detail. Under stationary conditions Eq. (1.1) $(j_{VV} + j_{VT} = 0)$ is written

$$\frac{\partial X}{\partial E} (1+\xi) + X \left(\beta_{\mathbf{V}} - 2\beta_0 X_e \frac{E}{A\omega} + \tilde{\beta}_0 \xi\right) = 0, \qquad (1.13)$$

where $F(E) = k_{VT}(E)/k_{VV}(E)$. After integration, the solution of (1.13) can be presented in the form⁷

$$X^{(0)}(E) = B \exp\left[-\beta_{\rm v} E + \beta_{\rm 0} X_{\rm o} \frac{E^2}{\hbar\omega} - \frac{\widetilde{\beta}_{\rm o}}{A(T_{\rm o})} \ln\left(1+\xi\right)\right], \quad (1.14)$$

where $\xi(E) = \exp\{A(T_0)[E - E^*(T_0)]\}$; the parameters $A(T_0)$ and $E^*(T_0)$ are given in Ref. 50 for a number of molecules. We note that the population (1.14) can be brought to a discrete form consistent with the results of Refs. 37 and 63-65. By way of example, Fig. 1 shows the $X^{(0)}(E)$ distribution in nitrogen. The accompanying comparison with the results of Refs. 49 and 66 shows that the assumption that the VT relaxation contribution is significant only at $k_{\rm VT}(E) > k_{\rm VV}(E)^{66}$ results in a high value for $X^{(0)}(E)$, while the purely classical approximation of the relaxation fluxes ($\beta_0 = \beta_0$) gives a high contribution from VT relaxation and lowers the population.⁴⁹

Simultaneous consideration of VV, VT, and eV processes within the framework of the present diffusion theory was analyzed in detail in Ref. 55. We note only that integration of the corresponding stationary equa-



FIG. 1. Population of vibrationally excited states of nitrogen molecules at $T_{\rm V}$ = 3000 K and T_0 = 900 K. 1) According to Boltzmann; 2) according to Treanor⁴⁸; 3) according to Brau⁵⁸; 4) according to Brau⁴⁹; 5) present calculation⁵⁰; 6) distribution function for the heavy isotope.⁶²

tion is more complicated than in the case of (1.13). Numerical machine computation of this case over a broad range of the parameters was described in Ref. 54.

Also of special interest is calculation of relaxation processes in mixtures (with VV' relaxation), which makes it possible to describe the isotope effect in the kinetics of nonequilibrium plasma-chemical reactions.^{38,59-61} A typical vibrational distribution function for an isotope mixture is shown in Fig. 1.⁶² We see that the vibrational-level population of the heavy admixture is noticeably higher on the initial X(E) segment. On the other hand, the function X(E) for the heavy component (usually a small admixture) is determines by VV' exchange, the rate of which, owing to the resonance defect, is lower than that of VV exchange, which determines the population X(E) for the light component. Accordingly, the distribution function for the heavy component is broken off earlier by VT relaxation, as can be seen clearly in Fig. 1.

Let us now proceed to description of the influence of chemical reactions on the shape of the vibrational distribution function. The condition for validity of the diffusion being considered here places limits on both the vibrational temperature and the region of the vibrational spectrum:

$$\hbar\omega < T_{\mathcal{X}} < \sqrt{\frac{T_0 \hbar \omega}{X_e}}, \quad E < (\beta_0 X_e)^{-1}, \quad \xi(E) < 1.$$
(1.15)

Nevertheless, the admissible energy range is still broad enough for use in calculating the rate constants of plasma-chemical processes. The primary reason for this is that, in contrast to the dissociation of diatomic molecules, which usually takes place at high vibrational energies $E > E^{*}[\xi(E) \gg 1]$ and has been analyzed quite fully,^{34,36} endoergic exchange reactions usually come about at $E < E^{*}$, i.e., at energies at which $\xi(E) \ll 1$. To consider the influence of the reaction on the form of the distribution function on the basis of (1.1), we go over from the homogeneous equation (1.13) to the corresponding inhomogeneous equation:

$$\frac{\partial X}{\partial E} \left(1 + \xi\right) + X \left(\beta_{\rm V} - 2\beta_0 X_{\rm e} \frac{E}{\hbar \omega} + \tilde{\beta}_0 \xi\right) = -\frac{1}{D_{\rm VV}} J_{\rm R} \left(E\right).$$
(1.16)

Solution of Eq. (1.16) by variation of the constants

⁽¹⁾The superscript (0) indicates that the influence of reactions was not taken into account in calculating the population.

leads to the relation

$$X(E) = X^{(0)}(E) \left[1 - \int_{0}^{E} \frac{J_{\mathbf{R}}(\varepsilon) \, d\varepsilon}{D_{\mathbf{VV}} X^{(0)}(\varepsilon) \, (1 - \frac{\varepsilon}{2})} \right].$$
 (1.17)

This relation has been analyzed in detail^{50.55} and can be used with the known function $X^{(0)}(E)$ [see, for example, (1.14)] for self-consistent determination both of the population X(E), which takes the chemical process into account, and of the over-all rate of the chemical process itself. In particular, given sufficiently rapid diffusion along the vibrational spectrum

$$D_{\rm VV}(E_{\rm a}) \gg k_{\rm R} (E = E_{\rm a} + \hbar\omega) n_0 (\hbar\omega)^2,$$
 (1.18)

the reaction perturbs the distribution function $X^0(E)$ only weakly, and the over-all rate of the chemical process is determined by the trivial relation

$$W = n_0 \int_{E_0}^{\infty} k_{\rm R}(\epsilon) n_0 X^{(0)}(\epsilon) \,\mathrm{d}\epsilon.$$
 (1.19)

On the other hand, if diffusion is slow enough and the condition converse to (1.18) is satisfied, the vibrational population drops off sharply in the range $E \ge E_a$, in proportion to

$$\exp\left[-\int_{E_{0}}^{E}\frac{k_{\mathrm{R}}\hbar\omega\,\mathrm{d}\varepsilon}{D_{\mathrm{VV}}\left(1-\xi\right)}\right].$$

A particular case of such a distribution function appears in Fig. 7. In this case, when the process is limited by diffusion along the vibrational spectrum, the over-all rate of the plasma-chemical reaction can be written in the form

$$W = n_0 J_0 - n_0 \left[\int_0^{E_{\rm a}} \frac{\mathrm{d}\epsilon}{D_{\rm VV}(\epsilon) |X^{(0)}(\epsilon)|(1 - \frac{\epsilon}{2})} \right]^{-1}.$$
 (1.20)

We observe that direct comparison of the results (1.19) and (1.20) again leads us back to inequality (1.18).

Up to this point, everything has pertained to quasistationary vibrational distribution functions. In some cases, variation of the distribution function with time is important for description of the kinetics of nonequilibrium plasma-chemical processes. The resulting nonstationary problem has been solved numerically by computer for several cases.⁶⁷ Analytic solutions of nonstationary diffusion-theory problems present considerable difficulty, and thus far have been found only for occasional specific cases.^{43,55} Thus, assuming that the Treanor term has little influence, we have for VV exchange with a variable diffusion coefficient $D_{vv}(E)$ = $D_0 e^{-\delta_{vv}E}$

$$\frac{\partial X}{\partial t} = \frac{\partial}{\partial E} D_0 e^{-\delta_V \mathbf{y} E} \left(\frac{\partial X}{\partial E} + \beta_V X \right).$$
(1.21)

This equation reduces to an ordinary differential equation on introduction of the variable $\xi = D_0 t \delta_{VV}^2 \exp(-\delta_{VV} E)$:

$$\xi^{2}X_{\xi\xi} + X_{\xi} \left[1 - \left(2 - \frac{\beta v}{\delta v v} \right) \xi \right] - \frac{\beta v}{\delta v v} X = 0.$$
 (1.22)

In particular, $\xi \approx 1$ describes the propagation of the Boltzmann-population front, and when $\xi \ll 1$ we obtain the asumptotic solution

$$X(E, \xi) \sim \exp\left(-\frac{1}{\xi} - \beta_{\rm V} E\right). \tag{1.23}$$

On the whole, it is evident from relations (1.19) and

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FIG. 2. Energy efficiency of CO_2 dissociation under quasiequilibrium conditions vs. temperature and rate of quenching. 1) 10^6 deg/sec; 2) 10^7 deg/sec; 3) 10^8 deg/sec; 4) ideal quenching.

(1.20) that the rates of plasma-chemical processes are determined basically by the nature of the vibrational population; the dependence on the form of the specific elementary-event cross section is weaker and, in some cases (1.20), absent altogether. The essentially non-Boltzmann nature of the distribution function leads to high rates of reactions that proceed via vibrationally excited states of the reagents. High reaction rates make it possible to suppress energy losses to vibrational relaxation and reverse reactions and to reach extremely high energy-efficiency values. This effect is clearly illustrated by comparison of the energy going into dissociation of CO₂ in a glow discharge, where the process comes about via electronically excited states of the reagents and the energy yield does not exceed $2.5\cdot 10^{-2}$ molecule/eV, and in high-pressure nonequilibrium hf and microwave discharges, where the reaction proceeds through vibrationally excited states of the molecules and a yield of 0.27 molecule/eV is reached.¹³ Let us now use the general vibrational-kinetic characteristics that we have obtained to describe specific nonequilibrium plasma-chemical processes.

2. DISSOCIATION OF CO₂ IN A NONEQUILIBRIUM PLASMA

The role of vibrational excitation of molecules in bringing about highly efficient plasma-chemical reactions is clearly illustrated by the decomposition of carbon dioxide:

$$CO_2 \rightarrow CO + \frac{1}{2}O_2, \quad \Delta Q \approx 2.9 \text{ eV};$$
 (2.1)

here ΔQ is the minimum energy needed to accomplish the process (2.1).

Decomposition of CO₂ has been investigated in numerous experiments and in various discharge systems. For example, Ref. 72 reports a study of process (2.1) in thermodynamically nonequilibrium electric-arc plasmas. The maximum energy efficiency in this system was ~15%. The theoretical maximum efficiency of process (2.1) in a quasiequilibrium plasma has been calculated^{72,73} and found to be ~43% (Fig. 2). An increase in efficiency is possible, as discussed above, only on transition to nonequilibrium systems, where the bulk of the discharge energy input can be localized on preferred chemical-process channels. In the stationary

variant, nonequilibrium conditions are realized most simply in low-pressure systems.⁷⁴ However, the usually relatively high value of E/p in these systems predominantly results in dissociation via electronic excitation, and this lowers the energy yield of the process (specific characteristics of this dissociation channel appear in Figs. 3 and 4). Thus, the energy efficiency of the glow discharge (e.g., with a full cathode) is 0.6– 8%.^{75,172}

The highest efficiency of CO₂ dissociation via excitatation basically of electron states (~30%) has been observed in plasma-radiolysis experiments.^{77.78} A detailed discussion of this dissociation mechanism will be found in Refs. 1 and 7. The plasma-beam discharge has a special place among the low-pressure systems; here, probably due to a contribution of dissociation via vibrational excitation of the CO₂, the efficiency of the decomposition (2.1) ranges from $20\%^{76}$ to $50\%^{173}$

Higher efficiencies have been attained in mediumpressure systems. Thus, an efficiency of ~60% has been observed in a pulsed microwave discharge with a magnetic field under electron cyclotron resonance conditions at pressures of 30–100 Torr.⁷⁹ Similar efficiencies have been obtained under similar conditions in a nonequilibrium hf discharge.⁸⁰ The highest energy efficiency in the decomposition of CO₂ (~80%) was obtained in a nonequilibrium steady microwave discharge at medium pressure (50–200 Torr), where the energy input was ~3.7 eV molecule.^{13,80} These experiments will be described briefly below.

We note that this process of CO₂ dissociation in plasma is of great practical importance in metallurgy,⁶⁸ the chemical industry,⁶⁹ and in the production of new types of motor fuels.⁷⁰ Further, the carbon monoxide that is generated can be used in a thermocatalytic process for the production of hydrogen with practically no further expenditure of energy⁷¹:

$$H_2O + CO \rightarrow H_2 + CO_2, \quad \Delta Q \approx -0.4 \text{ eV},$$
 (2.2)

-which is especially important for atomic-hydrogen power engineering.



FIG. 3. Cross sections of dissociation of molecules via electronically excited states vs electron energy. $1-CH_4$; $2-O_2$; 3-NO; $4-N_2$; $5-CO_2$; 6-CO; $7-H_2$.

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0



Securing maximum efficiency is, as we noted above, dependent on conduct of the net process (2.1) via vibrationally excited states of the reagents, in accordance with the scheme

$$CO_2^* \rightarrow CO + O, \quad D = 5.5 \text{ eV}.$$

(2 2)

$$-\operatorname{CO}_2^* \rightarrow \operatorname{CO}_2, \quad \Delta Q = 0.3 \text{ eV}.$$
 (2.4)

To determine optimum conditions for the dissociation (2.3)-(2.4), it is necessary to analyze the kinetics and over-all energy balance of the process in the plasma.

a) Kinetics of dissociation of CO₂ via vibrational excitation of ground electronic state

At $T_e = 1-2$ eV, a major part of the discharge energy input is concentrated on excitation of the antisymmetric vibrational mode of CO_2 (allowance for an admixture of CO increases the concentration of energy on this type of vibration)^{81.82} (Fig. 5). Since, at the same time, the VT relaxation from this mode is relatively slow, it is the antisymmetric vibrations that basically determine the dissociation of the CO₂. Basically, the plasma electrons excite lower vibrational levels of CO₂; population of the states that participate in the chemical event of decomposition takes place for the most part in the VV relaxation process. Population of states with energies sufficient for dissociation along the antisymmetric mode $[D(CO_2) = 5.5 \text{ eV}]$ is prevented by VT and intermode VV' relaxation process. But when $E < D(CO_2)$, the contribution of these collisional relaxation processes is found to be relatively small (Fig. 6) owing to the smallness of $D(CO_2)$ compared to



FIG. 5. Distribution of energy lost by electrons in CO_2 among excitation channels.



FIG. 6. Relaxation of antisymmetric CO_2 vibrational mode. 1) VV relaxation; 2) VT relaxation; 3) VV' relaxation: $T_{Vs}(K)$ =10³ (a), 2 · 10³ (b) and 3 · 10³ (c); 4) transition to mode equilibrium; a) uniform pumping of all types of vibrations; b) preferential pumping of antisymmetric mode; 5) energy of CO-O dissociation.

the energy necessary for dissociation of CO_2 via the adiabatic channel for the antisymmetric mode.⁸³

Before calculating the dissociation rate constant, we note that the frequency of dissociation is considerably higher than the frequency of population of states with energy $D(CO_2)$ in the process of VV exchange^{37 b)}:

$$P\omega_{\mathbf{a}} \gg k_{\mathrm{VV}} (D) n_0 (\delta_{\mathrm{VV}} \hbar \omega_{\mathbf{a}})^2;$$
(2.5)

here P is the probability of a nonadiabatic transition on dissociation. In the case of (2.5), the dissociation rate is limited by diffusion along the vibrational spectrum and is determined by relation (1.20). Here, recognizing that the vibrational temperature is the same for Fermi-resonant symmetric modes⁸⁴ and taking account of intermode anharmonicity⁸⁵ (the constant $x_{ess} = 12$ cm⁻¹), we may, neglecting dissociation, take the population of the antisymmetric mode in the form

$$X_{a}^{(0)} \approx \frac{1}{T_{Va}} \exp\left[-\frac{E}{\hat{T}_{Va}} + \frac{x_{ea}E^{2}}{\hat{T}_{b}\hbar\omega_{a}} - \frac{x_{eas}ET_{Vc}}{\hbar^{2}\omega_{a}\omega_{s}T_{0}} - \frac{1}{A} \ln\left\{1 \pm \exp\left[-\frac{A(E-E^{*})}{\hbar\omega_{a}}\right]\right\}\right];$$
(2.6)

here $x_{ea} = 5 \cdot 10^{-3}$ is the constant of anharmonicity of the antisymmetric vibrations and the diffusion-theory parameters A and E^* can be estimated^{37,50} for $T_0 = 300-1000$ K at $A \approx 0.5$ and $E^* \ge D(CO_2)$. The above function $X_a^{(0)}(E)$ enables us to determine both the final form of the vibrational population of the antisymmetric mode with dissociation [the results of a calculation of $X_a(E)$ with relation (1.17) appear in Fig. 7] and the rate constant of decomposition of CO_2 , expressed in terms of the normal probability distribution:

$$k_{\rm R}^{\rm a} \left(T_{\rm Va}, \ T_{\rm 0} \right) \approx k_{\rm VV} \left(D \right) \frac{(\hbar\omega_{\rm a})^2}{T_{\rm Va}} \sqrt{\frac{x_{ea}}{4\pi T_0 \hbar\omega_{\rm a}}} \left[\Phi \left(D \sqrt{\frac{x_{ea}}{T_0 \hbar\omega_{\rm a}}} -\frac{1}{T_{\rm Va}} \sqrt{\frac{T_0 \hbar\omega_{\rm a}}{x_{ea}}} \right) - \Phi \left(-\frac{1}{T_{\rm Va}} \sqrt{\frac{T_0 \hbar\omega_{\rm a}}{x_{ea}}} \right) \right].$$

$$(2.7)$$

We note that the expression for the rate of dissociation of CO₂ in terms of symmetric-mode excitation $k_{\rm R}^{\rm s}(T_{\rm Vs})$,

⁸⁾Here and consistently below, the subscripts "a" and "s" refer to antisymmetric and Fermi-resonance symmetric vibrational modes.





FIG. 7. Population of antisymmetric CO₂ vibrational mode.

 T_0) is qualitatively similar to the above, but becomes quantitatively less important at $T_{\rm Va} > T_{\rm Vs}$. The dissociation rate (2.7) then depends on two vibrational temperatures, and for this reason the above approximation is called the two-temperature approximation.^{80,87,89}

Above we described the dissociation of CO_2 in terms of excitation of the antisymmetric vibrations to the energy $D(CO_2)$ with a subsequent nonadiabatic ${}^{1}\Sigma^{*} \rightarrow {}^{2}B_2$ transition. However, it is necessary to consider the possibility of collisionless intramolecular VV' relaxation associated with intermode anharmonicity and the Coriolis interaction and resulting in mixing of various types of CO_2 vibrations. This effect is strongest when the intermode anharmonicity $x_{ess}v_av_s$ exceeds the resonance defect $\Delta \omega = 300 \text{ cm}^{-1}$. In the case of strongly selective pumping of the vibrations by electron impact, in which the average number of quanta on the symmetric modes is small:

$$\overline{v}_{s} < \frac{1}{x_{eas}} \frac{\hbar \omega_{a} \Delta \omega}{D(CO_{2})}, \qquad (2.8)$$

this relaxation has practically no influence on the dissociation of carbon dioxide via the antisymmetric mode (see Fig. 6). In this case, the rate of the process is described by (2.7); we shall call this the two-temperature approximation, since the dissociation rate is determined by two vibrational temperatures—antisymmetric and symmetric.

Let us now consider the contrary case, in which, as a result of a small difference in mode pumping for the vibrational energies:

$$E > \hbar \sqrt{\frac{\omega_a \omega_b \Delta \omega}{x_{cas}}} \approx 3\hbar \omega_a, \qquad (2.9)$$

separation of the populations by normal-vibration types makes no sense. The values of T_{\bullet} that correspond to this case are shown in Fig. 5. In this variant, when the modes are completely "mixed," it is impossible to speak of the populations of specific vibrational levels, but only of the vibrational-energy distribution f(E) of the molecules. The function f(E) depends on a single vibrational temperature, and for this reason we shall call this approximation the single-temperature approximation.⁸⁶⁻⁸⁸

To determine the distribution function f(E), it is again necessary to use the diffusion equation (1.1).

Here, however, in contrast to the single-mode case examined above, the density inhomogeneity of the vibrationally excited states along the energy axis is essential in writing the relaxation fluxes [the density of states $\rho(E) \sim E^{S-1}$ takes into account the effective number S of vibrational degrees of freedom of CO₂]. Also in the single-temperature approximation, in contrast to (1.6), the VV flux does not contain a term with anharmonicity, and diffusion is resonant in nature: D_{VV} $= k_{VV}^0 n_0 h \omega_s E (k_{VV}^0 \approx k_0 = 10^{-10} \text{ cm}^3/\text{sec})$. A detailed discussion of diffusion theory for the case of equilibrium of the CO₂ vibrational modes will be found in Refs. 86 and 87. Here the dissociation rate constant is obtained in the form

$$k_{\rm R} = \frac{k_{\rm VV}^0}{\Gamma(s)} \frac{D^s \hbar \omega_{\rm B}}{T_{\rm V}^{s+1}} \exp\left(-\frac{D}{T_{\rm V}}\right) \sum_{r=0}^{\infty} \frac{(s+r+1)!}{(s-1)! \, r!} \frac{\gamma(r+1, \Delta)}{(\beta_{\rm V}D)^r}; \quad (2.10)$$

here $\Gamma(s)$ is the gamma function, $\gamma(r+1, \Delta)$ is the incomplete gamma function, and $\Delta \leq \beta_V D$ [a small deviation of Δ from $\beta_V D$ results from elimination of the divergence of $f(E)^{BT}$ near zero energy]. The sum in the right-hand side of (2.10) depends weakly on β_V and Δ and, according to a machine calculation, $0.5\beta_V D \leq \Delta$ $<\beta_V D$ varies in the range 1.1-1.3 at $T_V = 1000-4000$ K.

It is interesting to note that the numerical values of the dissociation rate constant in the single-temperature (2.10) and two-temperature (2.7) approximations do not differ by very much. This is because the Treanor factor, which determines the deviation from the Arrhenius relation in the two-temperature approximation, is actually offset by the multiplier $(D/T_{\rm V})^{\rm s}$, which takes account of mode mixing in the single-temperature approximation.

Given that condition (2.5) or the analogous condition in the vibrational-mode equilibrium approximation is satisfied,⁸⁷ when the rate of the process is limited by VV relaxation, the rate constant is practically independent of the specific mechanism of the elementary event. Thus, for example, the final answers (2.7) and (2.10) pertain not only to the direct process (2.3), but also, and equally, to the formation of the intermediate stable ³B₂ state (Fig. 8), which collapses after disproportionation: $CO_2(^3B_2) + CO_2 - CO_3 + CO.^{90}$



FIG. 8. Diagram of lower electronic terms in CO₂ molecule.

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The rate constants (2.7) and (2.10) given above pertained to reaction (2.3), which limits the decomposition process. Here the total carbon monoxide yield is codetermined by the secondary reaction (2.4), which, by virtue of its endoergic nature, is also stimulated by vibrational excitation of the CO₂. Unfortunately, we do not yet have reliable information on the kinetics of this reaction under nonequilibrium conditions. Moreover, even our data on the activation barrier of process (2.4) are contradictory.⁸¹⁻⁸³ Nevertheless, estimate calculations indicate that even at $T_V \ge 0.1$ eV, the rate of this secondary process prevails over the main alternative channel-three-particle recombination of atomic oxygen.

b) Vibrational kinetics and energy balance of the CO₂ decomposition

Available data on the kinetics of dissociation enable us to write the balance for the effective number of quanta $n_{a,s} = [\exp(\hbar \omega_{a,s}/T_{Va,s}) - 1]^{-1}$ on the antisymmetric and symmetric modes. The energy-balance relations form a system of nonlinear equations that take into account vibrational pumping, relaxation, reaction, and energy exchange between modes^{80.89}:

$$\frac{dn_{a}}{dt} = k_{ev}n_{e}\theta \left(E_{V} - k_{ev}n_{e}\hbar\omega_{a}t\right) - k_{a}s(T_{0})n_{0}\left[n_{a}\left(1+n_{s}\right)^{3} - e^{-\delta/T_{0}}n_{s}^{3}\left(1+n_{a}\right)\right] - k_{R}^{a}\left(T_{Va}, T_{0}\right)n_{0}\frac{D}{\hbar\omega_{a}}, \qquad (2.11)$$

$$\frac{dn_{s}}{dt} = \frac{2}{3} k_{as} (T_{0}) n_{0} [n_{a} (1+n_{s})^{3} - e^{-\delta/T_{0}} n_{s}^{4} (1+n_{a})] - k_{VT}^{s} n_{0} [n_{s} - n_{s} (T_{Vs} = T_{0})] - k_{R}^{s} (T_{Vs}, T_{0}) n_{0} \frac{D}{\hbar \omega_{s}}, \qquad (2.12)$$

$$\frac{dT_0}{dt} = \gamma k_{\rm VT}^s (T_0) n_0 [n_s - n_s (T_{\rm Vs} = T_0)] \hbar \omega_s.$$
(2.13)

The interaction between the modes is specified in (2.11) and (2.12) by nonlinear multipliers that describe, in a harmonic approximation, the forward and reverse processes of conversion of a single antisymmetricvibration quantum to three symmetric valence-vibration quanta.^{37,94} Here $E_{\rm V}$ is the energy introduced into the discharge per molecule of CO₂, $\delta = 500$ K is the energy defect in decay of one antisymmetric quantum into three deformation quanta, $\gamma \approx 0.5$ is a coefficient related to the translational and rotational heat capacity, and $k_{\rm m}(T_0)$ and $k_{\rm VT}^{\rm s}(T_0)$ are the rate constants of energy exchange between the antisymmetric and symmetric modes and of the VT relaxation of the deformational vibrations, which is much stronger than the relaxation from other modes.^{37,74}



FIG. 9. Variation of principal temperatures of CO₂ in time at specific energy input $E_{\rm V}=0.5~{\rm eV}/{\rm molecule}$). $1-n_{\rm e}/n_0=3\cdot10^{-6}$; $2-n_{\rm e}/n_0=10^{-6}$; $3-n_{\rm e}/n_0=3\cdot10^{-7}$; $4-T_{\rm Va}$; $5-T_{\rm Vs}$; $6-T_0$.

Numerical solution of the system of nonlinear equations (2.11)-(2.13) enables us to follow the dependence of the three principal system temperatures T_{Va} , T_{Va} , and T_0 on time at various degrees of ionization and various specific energy inputs E_V . The results of a numerical calculation for $E_V = 0.5$ eV appear in Fig. 9. We see that the relative departure from thermal equilibrium T_{Va}/T_0 decreases with decreasing n_e/n_0 ; in addition, oscillation energy transfer between vibrational modes appears at relatively low degrees of ionization.⁹⁴

Knowing $E_{\rm v}$ and the final steady temperature ($T_{\rm Va} = T_{\rm Vs} = T_0$), we can determine the fraction of the vibrational energy that went into the chemical process and the fraction expended on translational degrees of freedom (we shall call the corresponding efficiency $\eta_{\rm VT}$ the relaxation efficiency). The dependence of $\eta_{\rm VT}$ on the degree of ionization at a fixed energy input $E_{\rm V} = 0.5$ eV is represented in Fig. 10. Figure 11 shows the similarly computed dependence of $\eta_{\rm VT}$ on $E_{\rm V}$ at a fixed degree of ionization [$\log (n_e/n_0) = -5.5$].

The basic qualitative aspects of the CO₂-dissociation energy balance can be traced clearly in an analytic calculation of the relaxation efficiency, which can be performed in the single-temperature approximation.⁸⁶⁻⁶⁸ Using expression (2.10) for the rate constant and remembering that $k_{\rm VT}(T_{\rm V}, T_0)$ depends weakly on $T_{\rm V}$, we write an equation that describes the variation of the average vibrational energy of the molecules

$$v_{\rm V}(T_{\rm V}) = \sum_{i} \frac{\varepsilon_{i} \hbar \omega_{i}}{\exp\left(\hbar \tilde{\omega}_{i}/T_{\rm V}\right) - 1}$$
(2.14)

and the translational temperature T_0 :

$$\frac{\mathrm{d}\epsilon_{\mathrm{V}}}{\mathrm{d}t} = k_{\mathrm{eV}} n_{\mathrm{e}} \hbar \omega_{\mathrm{a}} \theta \left(E_{\mathrm{V}} - k_{\mathrm{eV}} n_{\mathrm{e}} \hbar \omega_{\mathrm{a}} t \right) - k_{\mathrm{R}} n_{\mathrm{0}} D - k_{\mathrm{VT}} n_{\mathrm{0}} \hbar \omega_{\mathrm{s}}, \qquad (2.15)$$

$$C_{p} \frac{\mathrm{d}}{\mathrm{d}t} (T_{0}) = k_{\mathrm{VT}} (T_{0}) n_{0} \hbar \omega_{s}; \qquad (2.16)$$

here $k_{VT}(T_0) = k_0 \exp(-BT_0^{1/3})$, *i* is the number of the vibrational mode, and g_i is the degree of degeneracy. Equation (2.16) can be integrated to determine the time during which the translational temperature of the molecules rises from the initial value T_0^{in} to a certain final value T_0^{f}

$$t_{\rm VT}(T_0^{\rm in}, T_0^{\rm f}) = \tau_{\rm VT} \sum_{r=0}^{\infty} \frac{(3+r)!}{6r!} \frac{\gamma(r+1, \delta)}{(u_{\rm in})^r}; \qquad (2.17)$$

here $\delta = u_{in} - u_f$ and $u_{f,in} = B(T_0^{f,in})^{-1/3}$. The dependence of $t_{VT}(T_0^{in}T_0^f)$ on T_0^f at $T_0^{in} = 300$ K is shown in Fig. 12



FIG. 10. Relaxation efficiency of CO_2 dissociation vs degree of ionization ($E_V = 0.5 \text{ eV/molecule}$).



FIG. 11. Relaxation efficiency of CO_2 dissociation vs specific energy input. 1) single-temperature calculation: I, II, III) degree-of-ionization regimes (see below in text); 2) two-temperature calculation; 3) numerical calculation of total efficiency in single-temperature approximation; 4) experiments with microwave discharge^{13,80}; 5) hfc discharge^{80,95}; 6) hfi discharge.^{13,100}

on the basis of a calculation in Ref. 87, and actually determines the variation of the translational temperature with time. From relation (2.17) and Fig. 12 we can derive the characteristic vibrational relaxation time

$$\tau_{\rm VT} = \frac{1}{k_{\rm VT} (T_0^{\rm in}) n_0} \cdot \frac{3 c_p T_0^{\rm in}}{\hbar \omega_c} \frac{1}{u_{\rm in}}, \qquad (2.18)$$

such that at $t < \tau_{VT}$ the relaxation proceeds relatively slowly with a constant $k_{VT}(T_0^{in})$ and the temperature rises linearly with time, while a sudden explosive rise in translational temperature occurs at $t > \tau_{VT}$.

With the condition $k_{\rm ev}n_s\pi\omega_a > k_{\rm VT}(T_0^{\rm a}) \times n_0\pi\omega_s$, it follows from (2.15) that a steady-state value of the vibrational temperature is established after a time $\langle k_{\rm ev}n_s \rangle^{-1}$

$$T_{\rm V}^{\rm st} = D \ln^{-1} \left[\frac{k_{\rm VV}^6}{k_{\rm eV}} \frac{n_0 D \hbar \omega_{\rm s}}{n_{\rm e} T_{\rm V}^{\rm st} \Gamma(S) \hbar \omega_{\rm a}} \left(\frac{D}{T_{\rm V}^{\rm st}} \right)^s \right].$$
(2.19)

The total vibrational-pumping time of the molecules is determined by the expression

$$\tau_{eV} = \frac{E_V}{k_{eV} n_c \hbar \omega_a}.$$
 (2.20)

The energy stored in vibrational degrees of freedom continues to be used for the most part in the chemical reaction for a time τ_r (afterglow time) after pumping stops; during this time, T_v decreases from $T_v = T_v^{\text{st}}$ to $T_v = T_v^{\text{st}}$, which can be determined from equality



FIG. 12. Increase of translational temperature with time (single-temperature approximation).

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of the energy fluxes going into the chemical reaction and into VT relaxation:

$$T_{\nabla}^{\min} = D \ln^{-1} \left[\frac{k_{\nabla \nabla} D}{k_{\nabla T} \left(T_{\delta}^{s} \right) \Gamma \left(s \right) T_{\nabla}^{\min}} \left(\frac{D}{T_{\nabla}^{\min}} \right)^{s} \right], \qquad (2.21)$$

where T_{Ψ}^{*} is the translational temperature of the gas at $T_{\nabla} = T_{\nabla}^{\min}$, i.e., at the time the chemical reaction ends. We note that the value introduced for the critical vibrational temperature (2.21) describes an important qualitative feature—the threshold nature of the dependence of relaxation efficiency on specific energy input. Actually, the vibrational temperature is relatively low, $T_{\nabla} < T_{\nabla}^{\min}$, at specific energy inputs $E_{\nabla} < \varepsilon_{\nu}$ ($T_{\nabla} = T_{\nabla}^{\min}$), and the reaction rate is quite far below the rate of VT relaxation ($\eta_{\nabla T} \rightarrow 0$). The exponential dependence of dissociation rate on vibrational temperature results in an equally sharp efficiency increase as the energy input and, consequently, the vibrational temperature pass through the threshold value.

Integrating Eq. (2.15) for the case $t > \tau_{eV}$, we find the time to accomplish the reaction after vibrational pumping stops, i.e., the reaction time in the "passive" phase of the discharge:

$$\tau_p = \frac{1}{k_{\rm VT}} \left(\frac{r_{\rm v}}{r_{\rm 0}} \right)_{n_0} \frac{c_{\rm vib} \left(T_{\rm V}^{\rm vin} \right)^s}{D\hbar\omega_s} ; \qquad (2.22)$$

here $c_{\rm vib}(T_{\rm V}^{\rm mis})$ is the vibrational heat capacity. Comparing (2.18) and (2.22), we may draw the important conclusion that $\tau_{\rm r} \ll \tau_{\rm VT}$, i.e., the relaxation time in the afterglow is always smaller than the vibrational relaxation time.

The calculated characteristic times of the process: $\tau_{\rm eV}$ (2.20), the time of reaction in the active phase of the discharge, $\tau_{\rm r}$ (2.22), the reaction time in the afterglow, and, finally, $\tau_{\rm VT}$ (2.18), the vibration relaxation time—can be used to analyze the qualitative features of the relaxation efficiency as a function of degree of ionization. Accordingly, we shall distinguish and discuss in succession three regimes that differ in their degrees of ionization.

1) High degree of ionization

$$\frac{n_0}{n_0} \gg \frac{k_{\rm VT}(T_0)}{k_{\rm eV}(T_0)} \frac{E_{\rm V}Dn_{0_s}}{c_{\rm vib}\hbar\omega_a (T_{\rm V}^{\rm min})^s}.$$
(2.23)

In this case, the time scales array themselves in the following order:

$$\tau_{\rm ev}\left(\frac{n_{\rm e}}{n_{\rm o}}\right) \ll \tau_{\rm f} \ll \tau_{\rm VT}.\tag{2.24}$$

Here the translational temperature T_0^* at the end of the chemical reaction $(T_v = T_v^{min})$ is

$$T_0^{\star} = T_0^{\ln} + \frac{c_{\text{vib.}} (T_V^{\min})^{\star}}{Dc_r}$$
(2.25)

and differs only insignificantly (~80 K) from the initial temperature. In this case the relaxation efficiency

$$\eta_{\rm VT} = 1 - \frac{\epsilon_{\rm VD} \left(T_{\rm V}^{\rm min}\right)^{4}}{E_{\rm VD}} - \frac{\epsilon_{\rm V} \left(T_{\rm V} = T_{\rm V}^{\rm min}\right)}{E_{\rm V}}$$
(2.26)

is at maximum and, what is essential, does not depend on n_e/n_0 —a further increase in the degree of ionization no longer lowers the relaxation losses (see I in Fig. 11).

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2) Intermediate degree of ionization

$$\frac{k_{\rm VT}\left(T_0^{\rm in}\right)}{k_{\rm eV}\left(T_{\rm e}\right)} \frac{E_{\rm V}\hbar\omega_{\rm su}\,u_{\rm in}}{\beta_{\rm c}} \ll \frac{n_{\rm e}}{n_{\rm 0}} \ll \frac{k_{\rm VT}\left(T_0^{\rm s}\right)}{k_{\rm eV}\left(T_{\rm c}\right)} \frac{E_{\rm V}\hbar\lambda_{\rm s}}{c_{\rm vib}\,\hbar\omega_{\rm a}\left(T_{\rm V}^{\rm min}\right)^2}.$$
(2.27)

In this case the time scales

$$\tau_{\rm f} \ll \tau_{\rm eV} \left(\frac{n_0}{n_0}\right) \ll \tau_{\rm VT} \tag{2.28}$$

are such that the temperature begins to rise as the degree of ionization decreases:

$$T_{0}^{s} = T_{0}^{in} + E_{V} \frac{k_{VT} (T_{0}^{in}) \, \hbar \omega_{s}}{k_{eV} (T_{e}) \, \hbar \omega_{s}} \frac{n_{0}}{n_{e}}.$$
 (2.29)

Here the relaxation efficiency decreases together with the degree of ionization (see II in Fig. 11).

3) Low degree of ionization: $\frac{n_e}{n_0} \leq \frac{k_{VT} (T_e^{\text{in}})}{k_{eV} (T_e)} \frac{E_V \hbar \omega_a u_{\text{in}}}{3c_T T_e^{\text{in}} \hbar \omega_a}.$ (2.30)

In this case, relaxation prevails over vibrational pumping, $\tau_{eV} (n_e/n_0) \ge \tau_{VT}$, and the energy efficiency drops off sharply (see III in Fig. 11).

Figure 11 shows the final form of the $\eta_{vT}(E_v, n_e/n_0)$ relation for the three degree-of-ionization regimes in the single-temperature approximation. Comparing the results for η_{vT} in the single- and two-temperature approximations, we observe two characteristic differences. First, owing to the higher vibrational heat capacity, the threshold of the $\eta_{vT}(E_v)$ relation is somewhat higher in the single-temperature approximation and, second, since VT relaxation from the symmetric mode is more effective than relaxation from the antisymmetric mode, η_{vT} is somewhat lower at a given degree of ionization in the mode-equilibrium approximation.

The total efficiency of the system is influenced by the following factors in addition to the vibrational relaxation considered above:

a) losses to excitation of inefficient decomposition channels, especially to electronic excitation (the relative fraction of these losses is indicated in Fig. 5; we see that it is small at $T_{\bullet} \approx 1$ eV, $\sim 5-10\%$);

b) losses related to the relaxation of CO_2 on atomic oxygen [the rate of exchange between the antisymmetric and deformation modes, $k_{as}(T_0)$ is one-and-a-half to two orders of magnitude higher in this case]; the smallness of the atomic-oxygen concentration [O]/ [CO₂] enables us to neglect this effect when $T_v < 0.8$ eV;

c) the losses governed by the nonresonant nature of VV relaxation within modes owing to the anharmonicity of the vibrations (in the two-temperature approximation, this effect results in an efficiency loss $\sim x_{ea}D/\hbar\omega_a \leq 0.1$);

d) losses related to the excess of the activation barrier of reaction (2.4) over its enthalpy (this excess amounts to $0.2-1 \text{ eV}^{91-93}$ and cannot lower efficiency by more than 10%);

e) losses related to possible reverse reactions—the decomposition products CO and O_2 react basically by a branched-chain mechanism, the threshold of which is characterized by a rather high translational tempera-



FIG. 13. Variation of principal charged- and neutral-particle concentrations with time.

ture when dilution is taken into account; we note that the establishment of quasiequilibrium between the forward and reverse reactions with vibrational excitation of CO and $T_{\rm V} > T_0$ would lower the over-all efficiency by ~30%.⁶

A single-temperature numerical determination of the basic elementary reactions and the vibrational and translational energy balance was made with a computer⁸⁷ to find the total efficiency at a fixed degree of ionization. Among other things, the computation included vibrational relaxation processes on atoms and reverse secondary processes.⁹⁰ On the whole, the results confirmed the dominant influence of relaxation processes on the total efficiency and made it possible to find the temperature and the concentrations of the principal charged and neutral particles as functions of time (Fig. 13).

c) Experiments on the dissociation of CO₂ in nonequilibrium medium-and high-pressure plasmas

We indicated above that the highest energy efficiency of CO₂ decomposition is obtained under nonequilibrium conditions ($T_e \gg T_0$) with stimulation of the process by vibrational excitation of the ground electronic state of the CO₂ molecule. Here the optimum discharge parameters are: specific energy input $E_v \approx 1 \text{ eV/molecule}$ (~5 J/cm³ atom), electron temperature $T_e \approx 1 \text{ eV}$, degree of ionization $n_e/n_0 \geq 10^{-6}$. Below we shall consider certain specific types of medium- and high-pressure discharges in which near-optimum regimes developed.

1) Microwave discharges.^{13,80,95-97} Figure 14 shows a microwave reactor for the decomposition of CO_2 . Up to 1.7 kW of microwave radiation at 2400 MHz entered the 72×34 -mm rectangular waveguide. The reactor was a quartz tube 38 mm in diameter that crossed the waveguide perpendicular to its wider wall. The power input into the plasma was measured with a calorimetric load and a directional coupler that recorded the power reflected from the discharge. The power absorbed by the plasma ranged from 1.2 to 1.4 kW, depending on discharge conditions. The gas was fed into the reactor by a gas distributor that set up a tangential velocity component around the reactor axis. The discharge



FIG. 14. Schematic diagram of stationary plasma-chemical microwave apparatus. 1) Magnetron; 2) directional couplers; 3) reactor; 4) matched calorimetric load; 5) gas-delivery system; 6) sampling tap; 7) metering plate.

was separated from the tube walls and had the shape of a cylinder 20 mm in diameter and 30 mm high. These studies were made at reactor CO₂ pressures of 50 to 200 Torr and at gas flowrates of 0.25-0.5 literatm/sec, which correspond to specific energy inputs into the discharge of 1.4 to 0.7 eV/molecule of CO_2 . The quantitative yield of the product (CO, O_2) was determined by several independent methods-chromatographic, manometric with condensation of the CO₂, massspectrometric, metering-plate, etc. Under the conditions of the experiments, the conversion increased from 15 to 30% with increasing energy input: the average amount of energy going into dissociation was 3.8 eV/molecule of CO₂. When the energy input was reduced to $0.2 \text{ eV/molecule of CO}_2$, the efficiency dropped sharply, an indication that the process has a threshold.

Complete curves of the energy efficiency of CO_2 decomposition plotted against specific energy input and pressure appear in Figs. 11 and 15, respectively.

Diagnostic experiments were performed to confirm the nonequilibrium nature of the process and to establish the basic parameters of the plasma. The vibrational-level populations were determined from the vibrational emission spectra in the infrared (2.5-3.1 μ m). It was found that the temperature of the antisymmetric vibrational mode ($T_{v_a} \approx 4500$ K) is indeed higher than that of the symmetric mode ($T_{\rm Vs} \approx 1500$ K) and still higher than the translational temperature T_0 . The electron temperature was estimated ($T_e \approx 15\,000$ K) and the electron concentration measured $[n_{\bullet} = (6-8) \cdot 10^{12} \text{ cm}^{-3}]$ by means of two-frequency microwave interferometry. The translational temperature at the exit from the discharge zone was measured with a thermocouple and found to be ~800 K. Measurements of the temperature of the neutral component, aided by analysis of the rotational structure of molecular spectra and the Doppler



FIG. 15. Energy efficiency vs pressure at $E_v = 0.5 \text{ eV}/$ molecule. 1) Calculation⁹⁶; 2) experiment.⁸⁰

⁹⁾Because it is excergic, the reverse reaction $CO^* + O_2 \rightarrow CO_2$ + O is evidently weakly stimulated by vibrational excitation of carbon monoxide molecules in plasma.

broadening of the atomic-oxygen lines⁹⁶ also confirm that the discharge is far off equilibrium. Spatial inhomogeneity of the temperature field in the discharge was detected at the same time: a narrow central zone of the discharge was heated to 1100 K. On the whole, it is evident that the experiment described here did indeed bring about the aforementioned optimum dissociation regime, and that this was why such a high energy efficiency was attained. In particular, this made it possible to consider scaling of the above experiment, i.e., attainment of equally high efficiency under similar conditions, but in systems of considerably greater capacity and, consequently, productivity. This has now been done in a microwave discharge using 70-100 kW, where the efficiency exceeded 60%.99 Further increases in microwave plasmatron power will require gas-flow velocities through the reactor that approach the speed of sound in order to sustain the required departure from equilibrium; this will evidently call for the development and testing of nonequilibrium plasma-chemical discharges in gas dynamic nozzles.

2) High-frequency discharges.^{13,80,95,100,101} Here it is necessary to distinguish CO_2 dissoclation experiments in hfc (capacitative) and hfi (inductive) discharge systems. Since the electric field is much smaller for a given generator power in the hfi case, while similar values of the parameter E/p are required to sustain the discharge, the working pressure is lower in the hfi variant than in the hfc discharge.

Since the working pressures were $1-5 \text{ Torr}^{13,100}$ in the case of the hfi discharge, the specific energy input was relatively high, at 4-8 eV/molecule of CO₂, and the process efficiency was ~30% (see Fig. 11). On the other hand, the high specific energy input resulted in a high degree of conversion, ~70-90%.

Higher discharge pressures and, accordingly, lower specific energy inputs are obtained in hfc plasmachemical systems.^{80,95} Experiments were performed at frequencies of 60, 20, and 5 MHz at discharge powers ranging from 1 kW to several tens of kW in a quartz chamber. The hf discharge was struck between cylindrical stainless-steel electrodes. The working gas was fed in along the wall through a hole in the electrode in order to hold the discharge zone on the chamber axis. This zone was 1 cm in diameter and 8 cm long. In a reactor with electric-field excitation of the discharge, it was possible to raise the working pressure to 100 Torr and higher while maintaining nonequilibrium, to lower the heat load on the chamber walls, and to increase the gas flowrate significantly. Plotting the efficiency against working-gas flowrate at pressures of 30 to 75 Torr in the reactor produces a curve showing saturation in the range of flowrates above 0.2-0.25 liter-atm/sec (see Fig. 11). The efficiency maximum (40-60%) is reached at a pressure of 70 Torr in a CO₂ flow 0.3 liter-atm/sec, which corresponds to a specific energy input of 0.7-1.0 eV/molecule. Here the conversion efficiency was 15-20%.

3) Non-self-sustained discharge sustained by a heavycurrent relativistic-electron beam. ^{95,102,103} This type of discharge is characterized by lower specific energy inputs than the microwave and hf variants. In particular, this results from the fact that the pressures are higher than in the above cases, at 1-3 atm. The threshold effect in the dependence of energy efficiency on specific energy input is most conspicuous in this type of discharge. CO₂ is not decomposed in the discharge at specific energy inputs smaller than 0.25 eV/ molecule of CO₂. At energy inputs above the threshold value, CO₂ dissociation efficiency increases with energy input up to the maximum value obtained in the experiment (0.6-0.7 eV/molecule of CO₂). The maximum efficiency reached values around 14% in the experiments.^{95,102}

On the whole, these results of experiments with the dissociation of CO_2 in plasmas, and especially in non-equilibrium microwave discharges, demonstrate the feasibility of obtaining optimum carbon dioxide decomposition regimes in practice via vibrational excitation of the ground electronic state.

d) Complete dissociation of CO₂ and reduction of carbon in plasma

In addition to the process considered above, in which CO_2 is decomposed to carbon monoxide, the singlestage reduction of carbon in plasma is also important and interesting^{79,104}:

$$CO_2 \rightarrow C + O_2, \quad \Delta Q \approx 11.5 \text{ eV}.$$
 (2.31)

In addition to its chemical-engineering applications, the process (2.31) is interesting as a physicochemical model of the reduction of metals from their oxides and halides.⁶⁹

The complete dissociation (2.31) requires not only the decomposition (2.1), but also destruction of the carbon monoxide molecules, which is somewhat difficult because of the extremely high (~11 eV) bond energy of this molecule. The disproportionation process

$$CO^* + CO^* \rightarrow C + CO_2 \tag{2.32}$$

is important here. Its activation barrier, though quite high $(E_a \approx 6 \text{ eV})$, is smaller by almost a factor of two than the bonding energy of the carbon monoxide molecule.^{105,123} The high energy threshold is effectively overcome by the essentially non-Boltzmann nature of the population of the vibrationally excited states of CO^{10710} :

$$W = n_0 \iint_{E' + E' \ge E_{\mathbf{a}}} X^{(0)}(E') X^{(0)}(E') k_{\mathbf{R}}(E', E') n_0 dE' dE''; \qquad (2.33)$$

here $k_{\rm R}(E', E'')n_0$ is the frequency of the elementary event at fixed energies E' and E'', which are concentrated in the vibrations of the carbon monoxide molecule. A specific form of $k_{\rm R}(E', E'')$ can be prescribed, for example, within the framework of the statistical theory of bimolecular reactions, as in Ref. 107. Here $X^{(0)}(E)$ is determined within the framework of the diffusion theory (1.14). The integral of (2.33) can be evaluated by the method of steepest descent, assuming E^*

¹⁰⁾The contribution of disproportionation with the electronically excited CO ($a^{3}\Pi$) molecule is evidently significant only at relatively high electron temperatures.

 $< E_a < 2E^*$. The problem then reduces to finding the maximum of the exponent in the integrand of (2.33) along the line $E' + E'' = E_a$. This maximum occurs at two points: $E = E_{opt}$ and $E = E_a - E_{opt}$ ($E_{opt} > E_a/2$), which are defined by

$$E_{\rm opt} = E^* - \frac{1}{A} \ln \frac{1}{2\beta_0 X_e (2E^* - E_a)} \cdot$$
(2.34)

It is important that $E_{opt} < E^*$ at most of the parameter values considered (it can also be shown that $E_{opt} > E_r$ where E_r is the point of reversal on the plots of the vibrational-population logarithm⁵⁰). Problems in the kinetics of reactions in which two vibrationally excited molecules participate are discussed in greater detail in Ref. 50. Here we present only the rate constant of the disproportionation of CO as a function of the vibrational and translational temperatures:

$$k_{\rm R} (T_{\rm V}, T_0) = \frac{k_0}{\beta_{\rm V} E_{\rm a}} \exp\left[-\beta_{\rm V} E_{\rm a} + \beta_0 x_{\rm e} \frac{E_{\rm opt}^2 + (E_{\rm a} - E_{\rm opt})^3}{\hbar\omega} - \frac{2\beta_0 x_{\rm e} (2E^* - E_{\rm a})}{A\hbar\omega}\right].$$
(2.35)

Relation (2.35) reflects an important property of plasma-chemical reactions of vibrationally excited molecules: despite the fact that $E_a > E^*(T^0)$, the breakoff of the distribution function at $E > E^*$ due to VT relaxation does not influence the rate of the process, because the main contribution to the kinetics of the reaction comes from molecules having energies $E \approx E_{opt}$ $< E^*(T_0)$.

The non-Boltzmann corrections in the argument of the exponential function in (2.35) raise the rate constant by several orders of magnitude and make it possible to explain the available experimental results on the disproportionation of carbon monoxide.^{79,106,108,109} In general, the disproportionation proceeds quite vigorously in the CO plasma; experimental reduction of carbon directly from CO_2 in plasma is a much more complex problem. Here the process is complicated by the influence of the strong reverse reaction $CO_2^* + C$ -2CO,¹²³ which can be suppressed only if the discharge parameters are precision-adjusted in such a way as to ensure heterogeneous stabilization of the carbon on the discharge-chamber walls.¹¹⁾ This problem is discussed in detail in Ref. 69. Such parameters have been obtained experimentally in medium-pressure systems in a microwave discharge with a magnetic field operating under electron cyclotron resonance conditions; complete decomposition of CO_2 (2.31) and reduction of carbon were obtained.⁷⁹

3. PRODUCTION OF HYDROGEN IN NONEQUILIBRIUM PLASMA-CHEMICAL SYSTEMS

Direct decomposition of water vapor is the most natural method of producing hydrogen. However, a number of physical limitations, primarily the high vibrational relaxation rate of the H_2O molecule, make it difficult to use this process. We shall therefore consider below certain alternative methods for the production of hydrogen, some of them including a preliminary stage with CO_2 dissociation in plasma.

The high energy intensity of nonequilibrium plasmachemical systems and the high gas flowrates through the discharge result in a high specific productivity and, consequently, small outlays of metals and optimum bulk and weight characteristics in the plasma-chemical reactors. Plasma-chemical methods for the production of hydrogen are especially interesting from this standpoint within the framework of atomic-hydrogen power engineering. These methods have energy efficiencies approaching those of other electrical processes (thermoelectrochemical, electrolytic), and specific productivities several orders of magnitude higher.^{110,139}

Despite the special importance of plasma-chemical hydrogen-producing methods in solution of various applied problems, there have been comparatively few experimental studies of this problem. Until recently, these studies have related chiefly to the decomposition of hydrocarbons in the glow discharge and have been characterized by extremely low energy efficiencies.¹ Higher efficiencies have been obtained in recent years in experiments with direct decomposition of H₂O in glow and microwave discharges; they will be discussed in greater detail below.

a) Direct decomposition of water vapor in plasma

The direct decomposition of water vapor with production of hydrogen in a plasma,

$$H_2O \rightarrow H_2 + \frac{1}{2}O_2, \quad \Delta Q \approx 2.6 \text{ eV},$$
 (3.1)

can be brought about by various mechanisms. However, the highest decomposition efficiencies would be expected in systems in which the electron temperature is not high enough for strong excitation of the electronic state and most of the energy introduced into the discharge is concentrated on excitation of vibrational degrees of freedom and, in contrast to the case of CO_2 , on dissociative sticking of electrons in H₂O molecules. Figure 16 shows curves of the fractions of the energy that are localized in the various electron-molecule interaction channels as calculated approximately on the assumption of a Maxwellian electron energy distribution function.¹¹¹ We see that at $T_e \leq 1.5$ eV, the decomposition (3.1) should be determined basically by vibrational excitation, while dissociative sticking should become significant at higher temperatures.



FIG. 16. Distribution of energy lost by electrons in H_2O among excitation channels.

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¹¹⁾Heterogeneous stabilization can also be ensured by clustering in the volume, but this would involve additional difficulties in propagating and sustaining the discharge.¹⁷⁸⁻¹³¹

1) Decomposition of H₂O via vibrationally excited states of the reagents. In this case, the mechanism of hydrogen formation is determined by the following successive stages:

1) Excitation of lower H₂O vibrational levels (in contrast to the case of CO₂, it is difficult to indicate a preferentially pumped mode here¹¹⁹).

2) Population of high excited states in VV relaxation; here it is important that the rates of intermode exchange $\nu_1(A_1) \neq 2\nu_2(A_1)$ and Fermi-resonant vibration exchange $\nu_3(B_1) = \nu_1(A_1)$ are close to the rate of intr-mode VV relaxation,¹¹² so that the same temperature can be assumed for the various vibrational modes the strongest VT relaxation takes place from the mode $\nu_2(A_1)].$

3) The chemical reactions that determine the over-all process (3.1) take place by an unbranched chain mechanism initiated by the dissociation $H_2O \rightarrow H + OH$, the rate constant of which can be estimated as follows in the single-temperature approximation (2.10):

$$k_{\rm R} \approx k_{\rm VV}^{0} \left(\frac{D}{T_{\rm V}}\right)^{\rm S} \exp\left(-\frac{D}{T_{\rm V}}\right),$$
 (3.2)

where $D(H_2O)$ is the dissociation activation barrier. Termination of the chain occurs in a three-particle H-OH recombination with the constant $k_a = 3 \cdot 10^{-31} \text{ cm}^3/$ sec. Vibrational excitation of the water molecules stimulates chain-continuation reactions:

$$H + H_2 0^* \rightarrow H_2 + 0H, \quad \Delta H_1 = 0.6 \text{ eV}, \quad E_{a1} = 0.9 \text{ eV}, \quad (3.3)$$

$$0H + H_20^{\bullet} \rightarrow H_2O_2 + H, \quad \Delta H_2 = 2.6 \text{ eV}, \quad E_{a2} = 3.0 \text{ eV}.$$
 (3.4)

Here the rate of process (3.1) is determined by the length of the chain ($\nu \approx 10^2$ at $T_v = 0.5 \text{ eV}$, $[H_2O] = 3 \cdot 10^{18}$ cm^{-3 113,144}):

$$V_{\rm R} = k_0 \, [{\rm H}_2{\rm O}]^2 \, \sqrt{\frac{k_0}{k_{\rm a} \, [{\rm H}_2{\rm O}]}} \exp\left(-\frac{D + E_{\rm a1} + E_{\rm a2}}{2T_{\rm V}}\right). \tag{3.5}$$

Let us further consider the energy efficiency of the above water-decomposing and hydrogen-producing process. The over-all process efficiency η is determined by the energy loss η_{ex} in unproductive excitation channels in the discharge, the efficiency $\eta_{\rm chem}$, which is related to the losses in the excergic forward reactions and reverse reactions, and, finally, by the vibrational relaxation efficiency η_{VT} of the reaction.

1.1) Discharge efficiency. η_{ex} depends on T_{ex} and can actually be determined from the plot of Fig. 16.

1.2) The chemical efficiency of the chain process depends on the length of the chain:

$$\eta_{\text{chem}} \approx \frac{\Delta H_1 + \Delta H_2}{(1/\nu) (D - E_{a2}) + E_{a1} + E_{a2}}.$$
(3.6)

Numerically, $\eta_{chem} = 85\%$ at $\nu = 10^2$, as compared to $\eta_{\rm cher}(\nu=1) \approx 50\%$ in the absence of a chain process.

Chemical efficiency may also be lowered by reverse reactions involving free radicals. Thus, owing to the rather high threshold of reaction (3.4), the OH concentration may prove to be relatively high¹¹⁵:

$$\left\{\frac{[\text{OH}]}{[\text{H}_2\text{OI}]}\right\}^2 = \frac{k_0}{k_a [\text{H}_2\text{O}]} \exp\left(\frac{E_{a2} - E_{a1} - D}{T_V}\right).$$
(3.7)

The influence of the biradical reaction $OH + OH \rightarrow H_2O$

462 Sov. Phys. Usp. 24(6), June 1981 + O was described in Ref. 115; it limits the vibrational temperature. The most important requirement for sustaining the η_{ehem} that has been reached is suppression of the reverse reaction $OH + H_2 - H + H_2O$ ($E_{(-)} \approx 0.5 \text{ eV}/$ molecule), which limits the yield of the product and the temperature of the system:

$$\frac{[\mathrm{H}_2]}{[\mathrm{H}_2\mathrm{O}]} \ll \exp\left(\frac{E_{\iota,j}T_{\mathbf{V}} - E_{\mathbf{a},2}T_0}{T_{\mathbf{V}}T_0}\right). \tag{3.8}$$

This requirement is more rigid than that imposed by the explosion hazard of H2-O2-H2O mixtures, which is reduced by the parameters of the water at elevated pressures. Figure 17 shows the admissible temperature range. Reverse reactions lower η_{chem} sharply; an estimate of this effect is given in Ref. 6.

1.3) Energy losses in vibrational VT relaxation take place in both the active and passive $(n_e = 0)$ zones of the discharge. This loss channel may prove to be most conspicuous because of the anomalously high value of $k_{\rm VT} \approx 10^{-12} {\rm cm}^3/{\rm sec}$.¹¹⁶ Vibrational relaxation in the active discharge zone is ineffective when the rather rigid criterion

$$\frac{n_{\rm e}}{[\mathrm{H}_2\mathrm{O}]} > \frac{k_{\rm VT}}{k_{\rm eV}} \tag{3.9}$$

is satisfied. Meeting condition (3.9) makes it possible to raise the vibrational temperature above the critical value:

$$T_{\rm V}^{\rm min} = \frac{D + E_{a1} + E_{a2}}{2\ln\left(\frac{k_0}{k_{\rm VT}} - \frac{E_a + E_{a2}}{\hbar\omega} \sqrt{\frac{k_0}{k_a (\rm H_{2}O)}}\right)},$$
(3.10)

at which the reaction rate becomes equal to the relaxation rate. The dependence of η_{VT} on the specific energy input E_v with allowance for losses in the active and passive discharge zones, and also the limits on the overall heating of the mixture when condition (3.9) is satisfied, are given in Refs. 114 and 115. In this case, in exactly the same way as in the dissociation of CO_2 , the $\eta_{\mathbf{VT}}(E_{\mathbf{V}})$ relation is of distinctly threshold nature (the threshold is, of course, determined by the critical value T_{V}^{min} of the vibrational temperature).

Estimates of the efficiency components can be used to follow the dependence of the total energy efficiency $(\eta = \eta_{ex}\eta_{ehem}\eta_{VT})$ on specific energy input in the case of a dissociation mechanism with vibrational excitation (Fig. 18).^{114,115} The figure shows that this relation is roughly similar in form to the corresponding curve for CO₂ (see Fig. 11).

23 0.2 a 300 300 1500 To.K

FIG. 17. Temperature limitation in direct decomposition of water vapor via vibrational excitation of molecules in plasma.

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*τ*_ν,•ν

2) Contribution of dissociative sticking to the decomposition of $H_{\circ}O_{\circ}$ At $T_{e} \ge 1.5$ eV (see Fig. 16), a considerable fraction of the energy may be concentrated on dissociative sticking of electrons to water molecules. The attainment of high energy efficiency in this plasma-chemical reaction channel (Fig. 19) is limited by the loss of an electron in the elementary chemical event. Here it is essential that the transition from the electron to the negative ion sharply accelerates recombination and actually results in the loss of energy (\geq 30 eV) that was previously expended on formation of an electron-ion pair.^{19,155} Dissociative sticking becomes energetically effective only when an electron formed in the plasma can participate in the reaction more than once. This process is possible in the presence of an effective channel in which negative fragment ions are destroyed (and an electron released) at a rate exceeding the rate at which they are lost in the fast ionion recombination process. In addition to associative unsticking,^{17,18} destruction of negative ions by electron impact is found to be effective in a number of cases (Fig. 20).^{117,118} For example, repeated utilization of one electron in dissociative sticking in the decomposition of H_2O is possible in the chain process^{20,120}

$$e + H_2O \xrightarrow{a} H^- + OH, H^- + e \rightarrow H + 2e.$$
 (3.11)

Under the action of a heavy-current relativistic-electron beam (REB), for example, the dissociative-sticking multiplicity μ [length of chain (3.11)] is determined by the degradation-cascade method¹²¹:

$$\mu \approx \int_{0}^{I} \varepsilon Z(\varepsilon) d\varepsilon \cdot \left(\varepsilon_{n} \int_{0}^{I} Z(\varepsilon) d\varepsilon\right)^{-1}, \qquad (3.12)$$

where I is the ionization energy and $Z(\varepsilon)$ is the REB degradation spectrum in a molecular gas $[Z(\varepsilon)d\varepsilon]$ is proportional to the average number of electrons that had an energy ε in the deceleration process]. For $\varepsilon \leq I$, the degradation spectrum can be represented approximately in the form¹²²

$$Z(\varepsilon) \approx 2\left(1+\frac{\varepsilon}{T}\right)^{-4} \ln\left(2+\frac{\varepsilon}{T}\right) + \left(1+\frac{\varepsilon}{T}\right)^{-2}.$$
 (3.13)

On substitution of (3.13) into (3.12), we obtain the multiplicity $\mu \approx 1$, which is actually limited by the energy of the subthreshold electrons. Larger μ are possible in electrical discharges, where the multiplicity of use of a single electron is limited by termination of the



FIG. 18. Energy efficiency and degree of conversion of water vapor in plasma. 1) Calculation; 2) experiments at pressures p(Torr) = 35 (3), 40 (4), and 60 (5).



- 1 a 🖬

FIG. 19. Cross sections of dissociative sticking of electrons to various molecules. 1) CO; 2) H_2O ; 3) O_2 ; 4) CO_2 ; 5) H_2 ; 6) I_2 .

chain (3.11) in ion-ion recombination $(H^{-} + H_2 O^{+} \rightarrow H_2 + OH; k_r^{ii} \approx 10^{-7} \text{ cm}^3/\text{sec})$ and the ion-molecule reaction $(H^{-} + H_2 O^{-} H_2 + OH^{-}; k_{i0} \approx 10^{-9} \text{ cm}^3/\text{sec})^{20.120}$:

$$\mu \approx \frac{k_d + k_1^{i_1} + k_{10} ([H_2 O]/n_e)}{k_1^{i_1} + k_{10} ([H_2 O]/n_e)};$$
(3.14)

here $k_d \approx 10^{-6} \text{ cm}^3/\text{sec}$ is the rate constant of H⁻ destruction by electron impact. To attain $\mu \gg 1$ in this case, it is necessary to have a high degree of ionization:

$$\frac{n_{\rm c}}{[{\rm H}_2{\rm O}]} > \frac{\kappa_{i0}}{k_{\rm d}}.\tag{3.15}$$

The efficiency of the process has been calculated for condition (3.15),^{20,120,111} and the results appear in Fig. 18. Here we observe only that the threshold of the $\eta(E_v)$ relation is much lower in this case than in the case considered under the preceding heading.¹¹¹

Thus, it has been shown that the decomposition of water vapor and the production of hydrogen in a plasma can be conducted with efficiencies of 50-70%. To obtain such high efficiencies, however, it is necessary to meet rather stringent requirements in the discharge. Whether the H₂O is decomposed via vibrationally excited states of the reagents or via dissociative sticking, the main limitation is the requirement that the degree of ionization be quite high. For different physical reasons, conditions (3.9) and (3.15) result in the same limit on the electron concentration: $n_{\bullet}/[H_2O] > 3 \cdot 10^4$, which would appear difficult to bring about at $T_{\bullet} = 1-3$ eV in experimental medium-pressure systems.

b) Experiments with direct decomposition of H₂O in plasma

The above rigid limitations on the parameters of the discharge in H_2O vapor make it difficult to attain the



FIG. 20. Destruction of negative ions by electron impact.

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highly efficient decomposition regimes considered above in practical experiments. In the glow discharge, for example, the maximum efficiency was ~12%.¹²⁵ In the medium- and elevated-pressure variants, obtaining the necessary degree of ionization at $T_{e} = 1-3$ eV will evidently require the use of non-self-sustained volume discharges sustained by heavy-current relativistic electron beams¹⁰² or plasma radiolysis by nu-clear-fission fragments.¹²⁴ At this time, the highest energy efficiencies in plasma-chemical decomposition of water (40%) have been obtained in a nonequilibrium microwave discharge with a scheme similar to that described in subsection c) of Sec. 2 (see Fig. 14). Let us discuss this experiment in greater detail.¹¹¹ The water-vapor flow from the evaporator to the reactor was varied from 0.35 to 1.6 liters-atm/sec. The upper limit of this flow was determined by the output of the evaporator, and the lower limit by the discharge jumping to the reactor wall. A water-cooled heat exchanger was installed at the reactor output to lower the temperature of the reaction products. The discharge was stable at pressures from 35 to 60 Torr. The microwave power put into the discharge was measured calorimetrically with a water load, and amounted to 1.2-1.7 kW.

Mass spectrometry and chromatography were used to analyze the products. They were hydrogen and oxygen in stoichiometric proportions. Simultaneous measurements of the power absorbed by the plasma, of the flowrate of the $H_2 - O_2$ gas mixture, and of the H_2O flowrate through the reactor made it possible to determine the plasma-chemical efficiency of dissociation and the conversion ratio of the water vapor in the system. Figure 18 shows the basic $\eta(E_v)$ relations obtained in the experiment at various pressures. Comparison with the calculated results shows that in this case the production of hydrogen was most probably supported by dissociative sticking. In addition to the position of the $\eta(E_{\mathbf{v}})$ threshold, this conclusion is also supported by the increase in energy efficiency with decreasing reactor pressure at a given energy input (a pressure decrease results in increases of E/p and T_{e} , which ultimately increases the fraction of energy expended on dissociative stocking; see Fig. 16). The fact that the efficiency limit reached in this experiment (~40%) is still below the theoretical maximum can be explained by the fact that the degree of ionization in the system was evidently not high enough to suppress the ion-molecule reaction $H^+ + H_2 O^- H_2 + OH^-$ [see (3.15)]. A small increase in the electron temperature in the system (obtained by raising E/p) would apparently raise the efficiency of the main experiment both by increasing the degree of ionization and by increasing the fraction of the energy localized on dissociative sticking of plasma electrons to H₂O molecules.

c) Production of hydrogen in nonequilibrium H₂O-CO₂ plasma-chemical systems

The direct decomposition of H_2O vapor in a nonequilibrium plasma comes up against limitations associated with the degree of ionization (3.9), (3.15) and with the action of the OH radical. Both of these limitations are

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FIG. 21. Mixture-composition limits and energy efficiency in production of hydrogen in CO_2 -H₂O plasma-chemical systems.

relaxed significantly when CO_2 and its decomposition product CO are added to the system. In fact, the presence of carbon monoxide in the system lowers the concentration of free OH radicals in the practically threshold-free reaction OH + CO - H + CO₂; on the other hand, CO and CO₂ have cross sections for vibrational excitation by electron impact that are two orders of magnitude larger than that of H₂O, and this makes it possible to lower the degree-of-ionization requirement significantly. Essentially, CO₂ may act as a physical catalyst for the production of H₂ from H₂O in plasma and, without being depleted, eliminate the difficulties that arise in decomposing pure water vapor.

1) Nonequilibrium plasma chemistry of the CO_2-H_2O mixture. The formation of hydrogen in a CO_2-H_2O mixture may proceed in accordance with the following mechanism. The decomposition of CO_2 to CO (2.1) follows the kinetics described in Sec. 2. The greater part of the atomic oxygen enters into reaction with CO_2 molecules [see (2.4), activation barrier E_x], but some of the oxygen atoms react with water vapor ($O+H_2O^*$ -OH+OH, $E_y \approx 1$ eV/molecule), initiating a chain process of reduction of molecular hydrogen:

$$OH + CO \rightarrow H + CO_{*}, H + H_2O^* \rightarrow H_2 + OH.$$
 (3.16)

The length of the above unbranched chain is found within the framework of the single-temperature approximation in the form¹¹⁵

$$\mathbf{v} = \frac{[\mathrm{CO}_2]}{[\mathrm{H}_2\mathrm{O}]} \exp\left(\frac{E_{\mathrm{y}} - E_{\mathrm{x}}}{T_{\mathrm{y}}}\right). \tag{3.17}$$

Clearly, hydrogen forms at a high rate when $\eta \gg 1$. However, vibrational excitation of the CO₂-H₂O mixture may result in the formation of various byproducts. The range of the parameters specifically corresponds to the production of hydrogen is limited primarily by the reactions OH + OH \rightarrow H₂O + ₀, H + CO₂ \rightarrow OH + CO, and H + ₀₂ \rightarrow OH + O. Figure 21 shows the admissible mixture compositions as a function of vibrational temperature.

The overall efficiency of hydrogen production in this system is determined basically by relaxation losses and losses in side chemical reactions. The relaxation losses limit the degree of ionization; Fig. 22 indicates the lowest admissible degrees of ionization in the CO-H₂O mixture. The losses in reverse reactions limit the parameter region in much the same way as indicated in Fig. 17. Calculated total efficiencies are shown in Fig. 21.¹¹⁵ We see that the efficiency may



FIG. 22. Degree-of-ionization limits in CO_2 -H₂O plasma-chemical systems.

reach ~60% in the optimum regime (energy consumption ~5 eV/molecule of H_2).

2. Nonequilibrium plasma chemistry of the $CO - O_2$ - H_2O mixture. Although the above process in the CO₂- H_2O mixture makes it possible to overcome the basic difficulties in direct decomposition of H₂O, it injects its own deficiency, which is typical of mixtures: a narrow region of admissible parameter values (see Fig. 21). Solution of this problem involves division of the single hydrogen-generating process into two stages. CO₂ is decomposed in the first stage (2.1) (the undecomposed dioxide is easily separated from the mixture), while in the second stage water vapor is added to the system and hydrogen is produced in a $CO-O_2-H_2O$ mixture (the two-stage cycle is closed with respect to the carbon dioxide, and it is not consumed in the overall pro $cess^{12}$). In describing the reactions in the CO-O₂- H_2O mixture we can distinguish three qualitatively different regimes. The first corresponds to a branch-ed-chain explosion, ¹²⁶ the second to slow oxidation of CO under the heterogeneous-catalytic action of H_2O ,¹²⁷ and, finally, the third regime is specific for the nonequilibrium plasma and hydrogen can be generated efficiently in it. The kinetics and energetics of this plasma-chemical regime were discussed in Ref. 115. The amount of energy consumed in production of hydrogen is shown in Fig. 23 for this case. The optimum energy expenditure is $\sim 1 \text{ eV/m}_0$ lecule, and the relative hydrogen yield $\sim 5\%$. Thus, the process is an interesting example of a plasma-chemical reaction in which the expenditure of electrical energy is smaller than the expenditure of "chemical" energy. Actually, ~1 eV is used to form one H₂ molecule, while the enthalpy of its formation is three times larger. Thus, the plasma functions not to feed energy into the reaction, but only to direct it into the necessary channel.

Thus, we have shown that these plasma-chemical systems can be used to produce hydrogen from water with about the same energy efficiencies, 60-70% (4-5 eV/molecule). Here the direct decomposition of water vapor is simplest from a physical standpoint, but it imposes very rigid requirements as to the degree of



FIG. 23. Energy consumption to produce hydrogen in plasma in a $CO-O_2-H_2O$ mixture.

ionization of the plasma. Introduction of additives (such as CO_2) makes it possible to relax electron-concentration requirements significantly, but on the other hand it narrows the range of admissible mixture composition.

4. SYNTHESIS OF NITROGEN OXIDES IN A NONEQUILIBRIUM PLASMA

The oxidation of atmospheric nitrogen in plasma is one of the most widely used plasma-chemical processes. It is especially interesting because nitrogen molecules can be vibrationally excited quite strongly by electron impact and are characterized by the lowest known vibrational relaxation rate (see Tables II and IV). The synthesis of nitrogen oxides in plasma is also an important example of the conduct of an endoergic chain reaction stimulated by vibrational excitation of the ground electron state of the molecules in the plasma.

The first studies of the plasma-chemical oxidation of nitrogen were carried out by Cavendish and Priestley in the electric arc at the end of the nineteenth century. The process was first put to use on an industrial scale by Birkeland and Eyde in 1900. The typical energy yield was ~25 eV/molecule of NO (efficiency ~4%). According to current conceptions, 145,146 an energy efficiency of ~11% is the best possible for thermodynamically quasiequilibrium systems (energy expenditure ~9 eV/molecule of NO); in principle, it can be obtained at pressures of 20-30 atm and temperatures of 3000-3500 K. We see that the energy efficiency is l_0w even at the optimum. Fixation of the oxides that are formed also requires high cooling (quenching) rates, $\sim 10^7 - 10^8 \text{ deg}/$ sec,¹⁴⁷ and it is difficult to obtain these rates in practice; as a result, it has not yet been possible to obtain NO yields exceeding 4-5% in an equilibrium plasma at expenditures smaller than 20 eV/molecule in real systems.

Beginning in the 1930's, the synthesis of NO in nonequilibrium plasmas was investigated experimentally in the glow discharge.¹⁴⁸⁻¹⁵¹ The efficiency of the synthesis remained low in these systems. Somewhat higher efficiencies were obtained in non-self-sustained discharges at atmospheric pressure that were sustained by heavycurrent relativistic electron beams.^{102,152} These experiments showed the threshold nature of the dependence of energy yield on specific energy input, with the threshold at ~0.1-0.2 eV/molecule (it is remarkable that there was practically no oxide yield at lower specific energy inputs in the similar experiments of Ref. 153). The

¹²⁾ The displacement reaction (2.2) which converts CO to H_2 thermocatalytically, is a more natural second stage of the cycle. However, the conduct of reaction (2.2) requires preliminary separation of the CO-O₂ mixture at a rate adequate to the first plasma-chemical stage (2.1), and this is a complex problem in itself.¹¹⁰

highest energy efficiency obtained in these systems is now about 14% (energy expenditure 7 eV/molecule of NO¹⁰²). Similar results were obtained in a pulsed microwave discharge with pulse widths of $5-10 \cdot 10^{-8}$ sec, a repetition frequency of 10^3 Hz, and pulse powers of 0.5-1.5 MW. Here the energy expenditure ranged up to 6 eV/molecule, which gives an efficiency of ~16%.¹ Higher energy efficiencies and degrees of conversion have been obtained in experiments conducted in a microwave discharge with a magnetic field^{79.142} and in plasma-beam¹⁵⁴ discharges, respectively. We shall discuss these experiments in greater detail in subsection f) of this section.

a) Mechanisms of oxidation of nitrogen in plasma

The nitrogen oxide synthesis

$$\frac{1}{2}N_2 + \frac{1}{2}O_2 \rightarrow NO, \quad \Delta Q \approx 1 \text{ eV}, \tag{4.1}$$

is determined in a plasma by the set of the elementary processes, among which the limiting processes are those in which the strong (~10 eV) bond of the N_2 molecule is broken:

1) Reaction with participation of vibrationally excited molecules in the ground electron states¹³⁾:

$$O(^{3}P) \rightarrow N_{2}^{*}(^{1}\Sigma_{g}^{*}, v) \rightarrow NO(^{2}\Pi) + N(^{4}S), \quad E_{a} \approx 3 \text{ eV}.$$
 (4.2)

This reaction follows excitation of low vibrational levels of N_2 and population of highly excited states in the VV relaxation process. The chain mechanism of the synthesis is then closed by the excergic reaction

$$N+O_2 \xrightarrow{h_2} NO+O, \quad \Delta Q \approx -1 \text{ eV}.$$
 (4.3)

2) Reactions via electron excitation are initiated by dissociation of nitrogen through the states $N_2(a^{i}\pi_{e}, B^{i}\pi_{e}, b^{i}\pi_{v})$ with a rate constant $k_d \approx 10^{-11}$ cm³/sec ($T_e = 1$ eV). Here the direct synthesis of NO takes place, for example, in the excergic process (4.3).

3) Dissociative recombination $(e + N_2^* \rightarrow N + N; k_r^{ei} \approx 10^{-6} \text{ cm}^3/\text{sec}$ at $T_e = 1 \text{ eV}$) also results in the formation of nitrogen oxides by further continuations of (4.3).

4) Ion-molecule reactions, e.g., $O^* + N_2 \rightarrow NO^* + N$ ($k_{10} = 10^{-11} - 10^{-12} \text{ cm}^3/\text{sec}$); further production of nitric oxide in (4.3) is also a possibility here.

The above synthesis mechanisms use sharply different amounts of energy. As in the case of dissociation of carbon dioxide, the energetically most efficient channel (4.2)-(4.3) involves vibrational excitation of the nitrogen, where most of the energy introduced into the discharge is concentrated (Fig. 24). At $T_e=1$ eV, this mechanism is much faster than the alternative channels because of the inequalities

$$k_{\rm d} \ll k_{\rm ev} \frac{\hbar\omega}{\Delta Q}, \quad \frac{n_e}{n_0} \ll \frac{k_{\rm ev}\hbar\omega}{k_{\rm e}^{\rm et}\Delta Q}, \quad \frac{[0^+]}{n_e} \ll \frac{k_{\rm ev}\hbar\omega}{k_{\rm lo}\Delta Q}.$$
 (4.4)

Below we analyze the elementary reaction (4.2) and the kinetics of the synthesis of nitrogen oxides in plasma

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FIG. 24. Distribution of energy lost by electrons in nitrogen among excitation channels. 1) Elastic losses; 2) vibrational excitation; 3) electron excitation; 4) ionization; 5) $T_{\rm V} \rightarrow 0$; 6) $\exp(-\hbar \omega/T_{\rm V}) = 0.2$; 7) $\exp(-\hbar \omega/T_{\rm V}) = 0.5$.

when the process is stimulated by vibrational excitation of molecules.

b) Elementary reaction of NO synthesis with participation of vibrationally excited nitrogen molecules

In contrast to the dissociation of CO_2 , where the rate of the process is limited by diffusion across the vibrational spectrum, the synthesis of nitrogen oxides is limited by elementary process (4.2), so that special interest attaches to its analysis (see subsection c).

Reaction (4.2) can be brought about as a direct (adiabatic, aMbNc in Fig. 25) or as a nonadiabatic reaction (aMb'Nc). The probability of the adiabatic channel can be obtained from the detailed balance principle⁸:

$$W_{a}(\nu) = \int_{0}^{\infty} \int F_{\nu}(\varepsilon_{T}, \varepsilon_{T}) \,\delta(\varepsilon_{T}' + E_{a} - \hbar\omega\nu - \varepsilon_{T}) \,\theta(\varepsilon_{T}') \\ \times \frac{e^{-\varepsilon_{T}/T_{0}} \sqrt{\varepsilon_{T}}}{\Gamma(3/2) T_{0}^{3/2}} \,d\varepsilon_{T} \,d\varepsilon_{T}';$$
(4.5)

here $\varepsilon_{\rm T}$ and $\varepsilon'_{\rm T}$ are the relative energies of translational motion before and after the reaction, Γ and θ are the Euler and Heaviside functions, and $F_v(\varepsilon_{\rm T}, \varepsilon'_{\rm T})$ is the translation-energy distribution of the products of the reverse reaction N + NO \rightarrow N₂(v) + O. If we use $F_v(\varepsilon_{\rm T}, \varepsilon'_{\rm T})$ in the form of the *a priori* function of the information-theory approximation¹³²

$$F_{\mathbf{p}}\left(\boldsymbol{\varepsilon}_{\mathbf{T}}, \ \boldsymbol{\varepsilon}_{\mathbf{T}}\right) = \frac{2\hbar\omega\varepsilon_{\mathbf{T}}}{\left(E_{\mathbf{a}} \div \boldsymbol{\varepsilon}_{\mathbf{T}}\right)^{2}} \boldsymbol{\theta}\left(E_{\mathbf{a}} \div \boldsymbol{\varepsilon}_{\mathbf{T}}^{\prime} \div \boldsymbol{\varepsilon}_{\mathbf{T}}\right)$$
(4.6)

to obtain an estimate, integration of (4.5) yields

$$W_{\rm a}(v) \approx \frac{1}{v^2} \exp\left[\left(\frac{E_{\rm a} - \hbar\omega v}{T_{\rm o}}\right) \theta\left(E_{\rm a} - \hbar\omega v\right)\right]. \tag{4.7}$$



FIG. 25. Possible pathways of NO synthesis reaction.

¹³⁾ The reaction $O({}^{1}D) + N_{2}^{*}({}^{1}\Sigma_{g}^{*}, v) \rightarrow NO({}^{2}\pi) + N({}^{2}D)$ is not significant in medium- and high-pressure nonequilibrium plasmas owing to the high rates of extinction of $O({}^{1}D)$ on nitrogen molecules.^{33,133}

We note that the statistical scatter of (4.6) is not quite characteristic for the adiabatic reverse-reaction channel, and $F_{\nu}(\varepsilon_{T}, \varepsilon_{T}')$ may be more deterministic, e.g., it may be possible to approximate it as a δ function. In this case, the probability of the adiabatic channel is obtained in the following form after integration of (4.5):

$$W_{a}(v) = \exp\left(-\frac{\hbar\omega_{v}}{T_{p}}\frac{\xi}{1-\xi}\right) \Theta\left(\frac{\hbar\omega_{v}}{1-\xi}-E_{a}\right); \qquad (4.8)$$

here $\xi \approx 0.3$ is the fraction of the energy of the exoergic reverse reaction that is transferred to translational and rotational degrees of freedom. Expressions (4.7) and (4.8) actually define the upper and lower limits of the probability of the adiabatic synthesis channel: numerically, for $\hbar\omega v \ge E_a$ and $T_0 \approx 10^3$ K, the probability is found to be rather low, $\sim 10^{-3} - 10^{-5}$. It is important that the adiabatic-channel probability [especially (4.8)] increases significantly with increasing T_0 . This effect is confirmed by a calculation of the adiabatic channel (4.2) by the classical-trajectory method in Refs. 30 and 134.

The nonadiabatic synthesis channel (4.2) results from the formation of an intermediate vibrationally excited c_{omplex} :

$$O(^{9}P) + N_{\perp}(^{1}\Sigma_{g}^{*}, v) \rightarrow N_{2}O^{*}(^{1}\Sigma^{+}) \rightarrow NO(^{2}\Pi) + N(^{4}S).$$
(4.9)

The first stage of the process (recombination) is characterized by the probability $^{\rm 32,135}$

$$W_{t}(v) = \frac{\pi V_{nn'}^{2}}{\hbar \Delta F} \sqrt{\frac{\mu}{T_{0}}} \left(\gamma^{2} v \right)^{E_{a}/\delta} \frac{1 - \exp\left\{ - \left(E_{a}/T_{0} \right) \left[1 - \left(T_{0}/\delta \right) \ln\left(1/\gamma^{2} v \right) \right] \right\}}{1 - \left(T_{0}/\delta \right) \ln\left(1/\gamma^{2} v \right)},$$
(4.10)

where $V_{nnr} = 100 \text{ cm}^{-1}$ is the matrix element of the interaction of the vibronic terms ${}^{1}\Sigma^{*}$ and ${}^{3}\Pi$ of the linear complex N₂O, ΔF is the difference between the slopes of terms ${}^{1}\Sigma^{*}$ and 3Π at their quasiintersection points.¹⁴⁰ γ is the change in the equilibrium N - N distance in the transition relative to the amplitude of the zero-point vibrations of N₂, μ is the reduced mass of the reagents, $E_0 = 0.8 \text{ eV}$ is the potential barrier on path aMb' (Fig. 25), and the parameter $\delta = 0.15 \text{ eV}$.³² The probability (4.10) is determined by the overlap integral $S_{\nu,\nu}$ of the vibrational wave functions of N₂ ($\nu \rightarrow \nu - \Delta \nu$) in the nonadiabatic transition¹³⁶:

$$S_{\boldsymbol{v}, \boldsymbol{v}-\Delta \boldsymbol{v}} = e^{-\gamma \mathbf{s}' \frac{(\boldsymbol{v}-\Delta \boldsymbol{v})!}{\boldsymbol{v}!}} \left(\gamma \sqrt{2}\right)^{\Delta \boldsymbol{v}} L_{\boldsymbol{v}-\Delta \boldsymbol{v}}^{\Delta \boldsymbol{v}} (2\gamma^2), \qquad (4.11)$$

where $L_m^{r}(x)$ is a generalized Laguerre polynomial. The problem of deriving the probability (4.11) was investigated in detail in Refs. 32 and 135 in an analysis of nonadiabatic transitions on a net of vibronic terms.

The second stage of (4.9)—breakdown of the intermediate complex—can be described within the framework of the statistical theory.^{35,137,138} This approach can be used because the characteristic time of energy exchange modes is small compared to the lifetime of the complex (this is aided by the nonadiabatic nature of the breakdown) and the frequency of the VT relaxation of N₂O^{*} is low compared to the frequency of reaction (4.9).¹³⁸ In the semiclassical Marcus-Rice approximation with corrections for anharmonicity, the probability of breakdown has the following form as a function of the vibrational $\hbar\omega v$, translational $\varepsilon_{\rm T}$, and rotational $\varepsilon_{\rm r}$ energies:

$$W_{2} = A_{\omega} \left[1 - \frac{2E_{a}X_{e}}{\hbar\omega(S-1)} \right] \left(\frac{\hbar\omega v - \varepsilon_{T}g_{T} + \varepsilon_{r}g_{T} - E_{a}}{\hbar\omega v + \varepsilon_{T}g_{T} + \varepsilon_{r}g_{r} - E_{0}} \right)^{S-1}.$$
 (4.12)

Here $A_{\omega} \sim 1$ is the frequency factor,³⁴ S=3 is the number of effective degrees of freedom of N_2O^* , and $g_{\overline{x}}g_{r}$ < 1 are parameters with which the conservation of total angular momentum is taken into account. It was shown in Ref. 57 that $g_{T,T} = 1 - (r_{1,2}/r^*)^2$, where $r_{1,2}$ are the maximum impact parameter of complex formation and the radius of the active molecule, respectively, and r^* is the characteristic radius of the activated molecule (since the complex forms nonadiabatically and the transition localized in a narrow range of N_2 - O distances, we have $g_r \approx g_T = g_0$). Figure 26 shows the $\sigma(u)$ curve (u is the velocity corresponding to ε_T) for a fixed total energy; it illustrates the preferential effect of vibrational energy on the rate of reaction (4.9). The relation obtained is similar to the result found by the classicaltrajectory method for the synthesis of NO via $O(^{1}D)$ $+ N_2^* ({}^1\Sigma_{e}^*, v)$, an indication that the statistical theory can be used to describe the elementary synthesis reactions.¹⁴¹ Finally, the probability of the nonadiabatic channel is written at relatively low temperatures T_0 $\leq 10^3$ K in the form

$$W_{\rm H}(v) \approx \frac{\pi V_{nn'}^2}{\hbar \,\Delta F} \sqrt{\frac{\mu}{T_0}} \left(\gamma^2 v\right)^{E_0/\delta} \exp\left(\frac{x_e E_0^2}{\delta^2}\right) \left(\frac{\hbar \omega v - E_0}{\hbar \omega v - E_0}\right)^{S-1}.$$
 (4.13)

The probability of the nonadiabatic synthesis channel is characterized by a weak dependence on T_0 and numerical values of ~10⁻² to 10⁻³. Comparison of (4.7), (4.8), and (4.13) indicates that the main synthesis channel at $T_0 \ge 10^3$ K is the direct adiabatic reaction and, conversely, when the plasma is off thermodynamic equilibrium and $T_0 < 10^3$ K, the nonadiabatic mechanism may be dominant. Numerical calculation by the classicaltrajectory method^{30,73,134} gave a value $T_0 \approx 2 \cdot 10^3$ K for the transition temperature.

For a nonequilibrium plasma at $T_0 \leq 1000$ K, therefore, the dominant mechanism of the elementary synthetic process may be (4.9), which is fundamentally different from the dominant mechanism under equilibrium conditions.

c) Population of highly excited states of the nitrogen molecule, and the rate constant of the synthesis

To determine the rate constant of process (4.9) at $T_{\rm V}$. > T_{0} , it is necessary to average the expression given above for the probability of the elementary process (4.13) over the vibrational distribution function. The vibrational population of the nitrogen molecule can then be written in the diffusion approximation (1.14) (see Fig. 1). The diffusion-theory parameters $A(T_{0})$ and $E^{*}(T_{0})$, which take VT relaxation into account, can be expressed for nitrogen in the form $A(T_{0}) = a/\hbar\omega\sqrt{T_{0}}$, $E^{*} = \hbar\omega[(1/4x_{0}) - b\sqrt{T_{0}}]$ where $a = 11 \text{ deg}^{1/2}$ and b = 0.38



deg^{-1/2}. It is important here that, in contrast to the case of CO₂ dissociation that was considered earlier, the vibrational population of the nitrogen molecules is only weakly disturbed by the chemical reaction of synthesis. The condition permitting neglect of the distortion of the vibrational distribution function is stated as smallness of the atomic-oxygen concentration and smallness of the probability of the elementary process relative to VV exchange:

$$\left(\frac{T_{\nabla}}{E_{a}}\right)^{S-1} \frac{[0]}{n_{0}} \ll \frac{k_{\nabla \nabla}(E_{a})}{k_{0}}.$$
(4.14)

The problem of rate-constant calculation is discussed in detail in Ref. 135. Here we present only the final results for the case $2x_eE_aT_V/T_0\pi\omega < 1$:

$$k_{\mathbf{R}} = \left[k_{0} \cdot \frac{4\pi V_{nn'}^{2}}{\hbar \Delta F} \sqrt{\frac{\mu}{T_{0}}} \left(\gamma^{2} \frac{E_{a}}{\hbar \omega}\right)^{E_{0}/0} e^{x_{0}E_{a}^{2}/0^{a}} \left(\frac{T_{\mathbf{V}}}{E_{a}}\right)^{S-1}\right] \times \exp\left(-\frac{E_{a}}{T_{\mathbf{V}}} + \frac{x_{0}E_{a}^{2}}{T_{0}\hbar\omega}\right).$$
(4.15)

We see that, in contrast to the dissociation of CO₂, the rate constant of the synthesis depends strongly on the characteristics of the elementary event. We note that the above relation does not consider the contributions of translational and rotational degrees of freedom to the rate of the synthesis reaction. Allowance for this effect would result in an additional multiplier $1 + (g_0 T_0/T_v)^{s-1}$, which differs little from unity at $T_v > T_0$. Relation (4.15) for the synthesis rate constant has been written in quasi-Arrhenius form with the argument of the exponential corresponding to the Treanor distribution. We note for subsequent numerical estimates that at $T_v = 3 \cdot 10^3$ K and $T_0 \le 10^3$ K, the pre-exponential factor in the square brackets amounts to $A_0 \approx 10^{-12} - 10^{-13}$ cm³/sec.

d) Kinetics and energy balance of the plasma-chemical synthesis of nitrogen oxides

The vibrational-energy balance equation can be represented in the following form for this case:

$$\frac{d\varepsilon_{\rm V}}{dt} = k_{\rm ev} n_{\rm e} \hbar \omega \theta \left(E_{\rm V} - k_{\rm ev} n_{\rm e} \hbar \omega t \right) - k_{\rm R} \left[O \right] E_{\rm a} - (k_{\rm VT} n_0 + k'_{\rm VT} \left[O \right]) \left(\varepsilon_{\rm V} - \varepsilon_{\rm V0} \right);$$
(4.16)

here ε_v is the average vibrational energy of the nitrogen molecule, which is related to temperature by Planck's relation (the conditions for validity of this relation with non-Boltzmann level populations are stated in Ref. 135) $\varepsilon_{v0} = \varepsilon_v \ (T_v = T_0)$, and the rate constants k_{VT} and k'_{VT} describe the relaxation of the nitrogen molecules on N2 and O, respectively. We note that since the N2-N2 VT relaxation is much slower than the $CO_2 - CO_2$ relaxation (see Table III), the effect of vibrational relaxation on atomic oxygen is strong in this case, in contrast to the case discussed in Sec. 2. Actually despite the low concentration of O atoms, the relaxation associated with them is of a nonadiabatic nature and has a rate comparable to that of the relaxation on nitrogen.33 Thus, both the reaction and relaxation rates depend on the concentration of oxygen atoms, which are formed by dissociative sticking $(k_a \approx 10^{-12}$ cm³/sec) and by direct electron-impact dissociation and are removed for the most part in the three-mole-

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cule ozonation reaction $(k_3 = 10^{-33} \text{ cm}^6/\text{sec})^{.138 \ 14)}$ Then the steady-state oxygen concentration is

$$[0]_{0} = \frac{n_{e}}{n_{o}} \frac{k_{e}}{k_{s}}$$
(4.17)

and, numerically for $n_0/n_0 = 10^{-5}$, equals $[O]_0 = 10^{16}$ cm⁻³. It is evident from (4.15) and (4.16) that the VT-relaxation losses can be neglected by comparison to the energy input into the reaction if the vibrational temperature exceeds the critical value

$$T_{\rm V}^{\rm min} = E_{\rm a} \ln^{-1} \frac{A_{\rm e} \exp\left(x_{\rm e} E_{\rm a}^{2} / T_{\rm o} \hbar \omega\right) \left[0\right] E_{\rm a}}{(k_{\rm VT} n_{\rm o} + k_{\rm VT} \left[0\right]) \hbar \omega}.$$
(4.18)

As in the dissociations of CO_2 and H_2O , this critical temperature determines the threshold of the dependence of energy efficiency on specific energy input. Generally, the existence of the critical temperature T_V^{\min} , like the threshold behavior of $\eta(E_V)$, is characteristic in all plasma-chemical processes that are stimulated by vibrational excitation. Then the steady-state value of the vibrational temperature is given by

$$T_{V}^{st} = E_{a} \ln^{-i} \frac{A_{0} \exp(x_{e}E_{a}^{i}/T_{0}\hbar\omega) [0] E_{a}}{k_{eV} n_{e} \hbar\omega}.$$
 (4.19)

VT relaxation can be neglected in the active phase of the discharge $(T_v^{st} > T_v^{min})$ if

$$\frac{n_{e}}{n_{0}} \gg \frac{k_{\rm VT}}{k_{e\rm V}} + \frac{k_{\rm VT}}{k_{e\rm V}} \frac{[0]}{n_{0}}.$$
(4.20)

When this condition is satisfied, the power put into N_2 vibrations is expended basically on the reaction, and the rate of the process in the active phase is

$$W \approx k_{\rm ev} n_{\rm e} n_0 \frac{\hbar \omega}{\Delta O}. \tag{4.21}$$

Numerically with $n_0 = 10^{14}$ cm⁻³ and $n_0 = 10^{19}$ cm⁻³, we obtain $W \approx 3 \cdot 10^{24}$ cm⁻³/sec, which is considerably higher than the rate of NO production in the alternative mechanisms (see Sec. 1). In the passive phase of the discharge, the oxide synthesis will continue owing to the presence of previously generated excited $N_2^*(^1\Sigma_{s}^*, v)$ molecules until the vibrational temperature has dropped from T_8^{vi} to T_8^{wis} . The energy-balance equation for the passive discharge phase is obtained from (4.16) by specifying the law according to which the atomicoxygen concentration falls: $[O] = [O]_0 \exp(-k_3 n_0 [O_2]t)$. This equation can be integrated analytically for temperatures above the critical point and times that are not sufficient for significant ozonation, ¹³⁸ giving the relation

$$T_{\mathbf{V}}(t) = T_{\mathbf{V}}^{\mathsf{st}} \left\{ 1 + \frac{T_{\mathbf{V}}^{\mathsf{st}}}{E_{\mathsf{a}}} \ln \left[1 + \exp\left(\frac{E_{\mathsf{a}}}{T_{\mathbf{V}}^{\mathsf{st}}} + \frac{x_{\mathsf{c}}E_{\mathsf{a}}^{*}}{T_{\mathsf{o}}\hbar\omega}\right) A_{\mathsf{o}}\left[\mathsf{O}\right]_{\mathsf{o}} \left(\frac{E_{\mathsf{o}}}{\hbar\omega}\right)^{2} t \right] \right\}^{-1}.$$
(4.22)

 \mathbf{From} this we find the reaction time in the passive phase:

$$\tau_{\rm p} \approx \frac{1}{k_{\rm VT} n_0} \frac{\hbar\omega}{E_{\rm a}}, \qquad (4.23)$$

we see that τ_p is smaller than the VT relaxation time. This means that the reaction can be brought about efficiently in the passive phase retaining the necessary degree of departure from equilibrium. Considering the similar results for CO₂ (subsection b of Sec. 2), we may conclude that the condition $\tau_p \ll \tau_{VT}$ is an im-

¹⁴⁾ Further oxidation of NO also contributes significantly at high oxide yields.

portant general qualitative property of nonequilibrium plasma-chemical processes stimulated by vibrational excitation.

Let us $n_0 w \ c_0$ nsider the efficiency of the synthesis, which it is convenient, as in the case of H₂O dissociation, to break up into three cofactors: $\eta = \eta_{er} \eta_{VT} \eta_{chem}$; here η_{ex} is the part of the efficiency governed by losses of energy in the discharge to unproductive excitation and ionization channels (Fig. 23 shows that $\eta_{ex} \approx 0.8-0.9$ at $T_e = 1$ eV), η_{VT} describes the VT relaxation losses, and $\eta_{\rm chem}$ is the chemical efficiency, which is related to the losses in expergic reactions. Given condition (4.20), η_{VT} is determined basically by the fact that in the passive phase, when T_v drops to T_v^{min} , practically all the remaining vibrational energy is used to heat the gas by vibrational relaxation. Actually, the energy expended on vibrational relaxation according to the energy balance for the passive discharge phase amounts to

$$E_{\mathbf{VT}} = \int_{T_{\mathbf{V}}^{\mathbf{I}_{\mathbf{0}}}}^{I_{\mathbf{0}}} \frac{(\hbar\omega)^{2} \mathbf{d} (\mathbf{1}/T_{\mathbf{V}})}{(e^{\hbar\omega/T}\mathbf{v}-\mathbf{1})^{s}} \left[1 + \exp E_{a}\left(\frac{\mathbf{H}}{T_{\mathbf{V}}^{\min}} - \frac{\mathbf{H}}{T_{\mathbf{V}}}\right)\right]^{-1}$$
(4.24)

and, accurate to terms of the second order of smallness $\hbar\omega/E_{z}$ equals $E_{v} = \varepsilon_{v}$ ($T_{v} = T_{v}^{min}$). On this basis, we obtain an estimate for the relaxation efficiency:

$$V_{\rm VT} \approx \frac{E_{\rm V} - \epsilon_{\rm V} \left(T_{\rm V} = T_{\rm V}^{\rm min} \right)}{E_{\rm V}}, \qquad (4.25)$$

which, of course, includes the threshold ($E_v \approx 0.5-0.8$ J/cm³-atm) determined by the critical vibrational temperature.

The chemical efficiency is sensitive to the specific mechanism of the process. The energy released into the products of the exoergic reaction (4.3) obviously cannot be used in useful reaction channels and goes into heating of the gas.¹⁵⁾ Even for a long chain (4.2)-(4.3), the chemical efficiency is limited to $\eta_{dhem} \approx 50\%$.

Figure 27 shows the total efficiency as a function of specific energy input¹³⁸ for comparison with experimental results obtained in various types of nonequilibrium discharges. We see that the principal feature of the plot, the $\eta(E_v)$ threshold, is confirmed qualitatively and quantitatively by experiment.

e) Stability of oxides to reverse reactions

It is convenient to distinguish two classes of reversereaction product losses. First there is the depletion of NO under the action of free atoms and radicals, which takes place as the plasma-chemical process advances, and then there is the decomposition of the "finished" product as a result of overheating at the exit from the system. Reverse reactions of the former type include the process $N + NO^{\frac{N}{2}} N_2 + O$, which is determined by atomic nitrogen. In a quasistationary



FIG. 27. Energy efficiency of synthesis vs specific energy input. 1) Calculation¹³⁵; experiments with microwave discharge; 2) Refs. 79 and 142; 3) Ref. 1; experiments with non-self-sustained discharges; 4) Ref. 102; 5) Ref. 152; 6) Ref. 153.

 $appr_{O}ximation$, the nitrogen-atom concentration varies during the passive phase of the discharge in accordance with the law

[N]
$$(t) = [O]_0 \frac{k_{\rm R} (T_{\rm V}, T_0)}{k_0} \exp((-k_3 n_0 [O_2] t)),$$
 (4.26)

where the variation of T_v with time is determined by relation (4.22). Writing the equation

$$\frac{\mathrm{d}\left[\mathrm{NO}\right]}{\mathrm{d}t} = -k_{\mathrm{N}}\left[\mathrm{NO}\right]\left[\mathrm{N}\right]\left(t\right) \tag{4.27}$$

for this reverse reaction and integrating it, we find the NO decomposition time τ_{diem}^{135} :

$$\frac{\tau_{\rm p}}{\tau_{\rm chem}} = -\frac{n_{\rm c}k_{\rm cV}}{n_{\rm o}k_{\rm VT}} \exp\left[-\frac{k_2}{k_{\rm N}} \left(\frac{E_{\rm a}}{\hbar\omega}\right)^2\right].$$
(4.28)

The depletion of nitric oxide in reverse reactions of this type is insignificant when $\tau_p/\tau_{\rm chem} \ll 1$, which is the case at the parameter values considered, with the oxygen temperature above 10³ K (see Ref. 138 for the various oxygen-excitation channels).

Reverse reactions of the second type-reactions of nitric oxide at the exit from the system (primarily $NO + NO \rightarrow N_2 + O_2$)—are characterized by comparatively high activation barriers and become significant only at $T_0 \ge 1500 \text{ K}$.¹³⁸ Statistical quasiequilibrium of the reactions $N_2 + O_2 \supseteq N_0 + NO$ is established by this overheating; its constant k_q can be expressed in terms of the standard thermodynamic constant k_p and the values of the equilibrium $X_e(E_q)$ and nonequilibrium $X(E_q)$ vibrational populations near the activation barrier:

$$k_{\rm q} (T_{\rm V}, T_0) = k_{\rm p} (T_0) \frac{X(E_a)}{X_{\rm e}(E_a)}.$$
 (4.29)

It is seen that when the subsystems are kept off equilibrium $[T_v > T_0 \text{ and } X(E_a) \gg X_e(E_a)]$, the existence of detailed balance of the forward and reverse reactions on several vibrational levels does not yet significantly lower the energy efficiency, $k_q \gg k_p$. However, the temperatures become comparable as vibrational relaxation progresses, with the result that the constant k_q tends to its equilibrium value, giving rise to significant energy-efficiency losses. We note that a kind of relaxation products is also significant here. Like VT relaxation, which results in establishment of a Boltzmann distribution and failure of nonequilibrium, this process can be described within the framework of statistical mechanics.^{143,144}

¹⁵⁾ The possible reaction $NO^* + O_2 \rightarrow NO_2 + O$, which uses the excited NO* molecule from reaction (4.3), results in branching of the synthesis chain and in an increase in [O], but has practically no effect on the energy characteristics of the process as observed in experiments in a microwave discharge with a magnetic field.^{79,142}

Assuming the absence of overheating above the temperature limit ($T_0 \leq 1500$ K), we obtain ~5 J/cm³-atm for the largest admissible specific energy input. Thus, the optimum process regime for medium- and elevated-pressure systems corresponds to an energy input of 2-3 J/cm³-atm (efficiency ~35%) and gives a relative oxide yield of 10-15%.

f) Experiments on the synthesis of nitrogen oxides in plasma

As we indicated above, the maximum energy efficiencies attainable in the synthesis of nitrogen oxides in nonequilibrium discharges (~35%) are low, compared, for example, to the dissociation of CO₂ and H₂O. This is primarily the result of irreversible energy losses in the exoergic stages (4.3) of the synthesis chain. However, as was evident from the brief review of experimental material given at the beginning of the present section, difficulties are encountered in attaining even this relatively low efficiency.

As of this writing, the highest energy efficiency in the synthesis of nitrogen oxide (~30%, energy consumption ~3 eV/molecule) has been obtained in a nonequilibrium microwave discharge with a magnetic field working under electron cyclotron resonance (ECR) conditions. Let us examine this experimental system, which is shown schematically in Fig. 28, in somewhat greater detail.^{79,142} The equipment worked both in a pulsed mode (with a magnetron radiation source) and in a continuous mode (in which case the source was a klystron) at pressures of 10 to 100 Torr $[N_2]:[O_2]=1:1$).

The magnetron generator ($\lambda = 3 \text{ mm}$) had a power of ~30 kW, a pulse duration of 0.3 μ sec, and repetition frequencies up to 10³ Hz; the klystron ($\lambda = 8 \text{ mm}$) had a power of ~30 W. Power was fed from the microwave generator to the reactor via a standard rectangularsection waveguide (7.2×3.4 mm). The reactor walls were cooled with liquid nitrogen to prevent a possible overheating of the system. The equipment produced the following range of discharge parameters: $n_e = 10^{12} - 10^{14} \text{ cm}^{-3}$, $T_0 = 600-1300 \text{ K}$, and $T_e = 1-2 \text{ eV}$.



FIG. 28. Diagram of microwave apparatus with magnetic field. 1) Reactor; 2) Wave-type converter; 3, 4) Solenoids; 5) Vacuum pump; 6) Nitrogen trap; 7) Refrigeration; 8) Gas cylinders; 9) Control volumes; 10) Vacuum gauge; 11,12) Differential manometers; 13) Directional coupler; 14) Spectrograph; 15, 16) Microwave detectors; 17) Semitransparent mirror; *M*) magnetron; *K*) klystron; *S*) diagnostic window.

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Under ECR conditions, the plasma absorbed over 90% of the power supplied, whereas in the absence of the magnetic field only 3-5% of the power was absorbed. We note that ECR not only optimizes the absorption of microwave energy, but also makes it possible to control the average energy of the electrons and, consequently, the degree of ionization. Detailed chemical analysis of the products, including mass spectrometry, showed a record-high synthesis energy efficiency of ~30%, which is near the theoretical limit, in pulsed operation under optimum conditions.

In an interesting experiment on the synthesis of nitrogen oxides in a plasma-beam discharge, a relatively high product yield (~20%) was obtained at a specific energy input of 2 eV/molecule and comparatively low energy efficiency (~10%).^{154,173} However, it remains unclear whether the synthesized oxides were stable in this system, where the translational temperature reaches several thousand degrees.

CONCLUSION

The above analysis of plasma-chemical process kinetics shows that the processes most promising from the standpoint of energy efficiency are those that proceed selectively via vibrationally excited states of the molecules with a considerable difference between the vibrational and translational temperatures. The theoretical calculations and the brief review of experimental results indicate that such processes are simplest to bring about in gases that admit of strong vibrational excitation and relax relatively sl_0wly-N_1 , CO, and CO₂. According to the data now available, the dissociation of CO₂ and the synthesis of nitrogen oxides are most effectively stimulated by vibrational excitation.

The energy efficiencies of plasma-chemical reactions stimulated by excitation of molecular vibrations depend strongly in turn on the conditions in the discharge. The highest efficiencies are attained in a narrow range of plasma parameters—the electron temperature must be held at around 1 eV and must be considerably higher than the translational temperature $(T_0 \le 10^3 \text{ K})$, the degree of ionization must be no lower than $10^{-7}-10^{-6}$ (in particular case of the decomposition of water, this requirement is several orders of magnitude more rigid), and, finally, the specific energy input should be 1 eV/molecule (~5 J/cm³-atm).

Practical realization of gas discharges with the parameters that ensure the best energy indicators is an independent and extremely complex problem that is beyond the scope of the present review. Nevertheless, considering the urgency of this problem, we offer a number of comments on the usefulness of specific types of discharges in bringing about the aforementioned optimum conditions in the plasma-chemical processes.

The requirements imposed on discharge systems in nonequilibrium plasma chemistry have much in $c_{O}mm_{O}n$ with the requirements that arise in the construction of powerful molecular-gas lasers. It is interesting that this parallel is legitimate in spite of the fact that the specific energy input is an order of magnitude higher

at the optimum in plasma-chemical systems as compared to laser systems. As in the case of molecular lasers, electric arcs of hf and microwave quasiequilibrium discharges, which usually involve high ($\geq 10^3$ Torr) pressures, offer little promise for initiating the processes discussed above, since it is not possible to obtain the necessary separation of the vibrational and translational temperatures.¹⁴ Low-pressure $(\leq 1 T_{0}rr)$ systems, where, despite the comparative simplicity of maintaining the nonequilibrium state (T_{\bullet}) $\gg T_0$), energy efficiencies are still low, are also for the most part unattractive in plasma chemistry. In the case of the traditional low-pressure, constant-field glow discharges, this results basically from the fact that the parameter E/p (at $pR \ll 10 \text{ T}_{0}\text{rr} \cdot \text{cm}$), which determines the electron temperature and the specific energy input E_v , is higher than optimum.^{156,157} As a result of this, on the one hand, the high values of E/pcause localization of a significant fraction of the power on unproductive electronic-term excitation channels and, on the other hand, the energy that has already been concentrated in molecular vibrations at "excessively high" energy inputs $(E_v \gg 1 \text{ eV})$ relaxes easily, sharply lowering the efficiency of the process. Similar effects lower efficiency in the low-pressure hfi discharges discussed in subsection c) of Sec. 2. We note that the pressures are higher $(10-50 T_0 rr^{158})$ in present-day glow discharges, which operate in a fast gas flow, and that the basic parameters are closer to optimum. In principle, the transition to optimum parameters in low-pressure systems is possible in the plasma-beam discharge, which has undergone intensive development in recent years.¹⁵⁹ In this discharge, beam instability results in transformation of electronbeam energy into plasma oscillations, the field of which heats the electrons to the necessary energy. Unfortunately, realization of the necessary optimum discharge conditions in these systems requires an extremely high level of Langmuir noise $\xi = E_2/4\pi n_e T_e$ $\geq (k_{eV}/k_{en})\hbar \omega/T_{e} \sim 0.1$ (where k_{en} is the rate constant of elastic scattering of electrons by molecules), while Langmuir noise with a level no higher than $\xi=10^{-2}-10^{-3}$ has thus far been recorded in experiments with beamplasma interaction at pressures $\leq 10^{-3} T_{O} rr^{160,171}$ In general, low-pressure systems are characterized by comparatively low specific productivity and by the use of large amounts of energy for gas transport, which makes them much less interesting from a technological standpoint.

Non-self-sustained atmospheric-pressure discharges sustained by relativistic electron beams (REB) or UV radiation appear most promising for the development of powerful gas lasers.^{161,164,167,188} They provide the necessary degree of ionization and electron temperature and maintain the necessary nonequilibrium conditions: $T_{\rm e}, T_{\rm V} \gg T_0$. An important advantage of these discharges is their spatial homogeneity. However, the specific energy inputs obtained thus far are still not high enough to make an approach to the optimum plasma-chemical regime. Nevertheless, the specific energy input has exceeded the critical threshold value in a number of experiments performed by the Physics Institute of the Academy of Sciences (FIAN),¹⁵² the Institute of Atomic Energy (IAÉ),¹⁰² and the State Scientific Research and Planning Institute of the Nitrogen Industry and Products of Organic Synthesis (GIAP).¹⁰³ and an efficient reaction stimulated by vibrational excitation was observed. The chief obstacles to higher energy inputs in such systems are instabilities, which are now under intensive study.^{162,163} Above we discussed pulsed or stable-frequency non-self-sustained discharges at atmospheric pressure; as concerns the analogous steady discharges, ^{169,170} their use is now limited by the low REB current densities and the resulting comparatively low degrees of ionization. Further improvement of steady atmospheric-pressure discharges may, in the future, make them the most interesting plasma-chemical systems from both the physical and the technological standpoints. This statement applies not only to non-self-sustained discharges sustained by REB, but also to other nonequilibrium, spatially homogeneous discharges excited at atmospheric pressure using subsonic and supersonic gas flows.¹⁶⁵

An important fundamental difference between plasmachemical and laser systems is that the former are not subject to such rigid requirements as to the spatlal homogeneity of the nonequilibrium discharge over the entire volume. Medium-pressure nonequilibrium hf and microwave discharges are interesting in plasma chemistry for this reason (see subsection c) of Sec. 2). Despite the lack of spatial homogeneity, it is these systems that have recently made possible the best approach to the optimum $n_{\rm e}/n_0$, $T_{\rm e}$ and $E_{\rm v}$, the initiation of reactions stimulated by vibrational excitation, and attainment of the highest energy efficiencies in the endoergic processes discussed in this review. Once past the difficulties of scaling these nonequilibrium discharges,¹⁶⁶ their powers can now be raised to 100 kW⁹⁹ while retaining high chemical-process efficiencies (up to 80%), so that they are even now tehcnologically promising.

To this brief comparative analysis of the various discharge schemes we should add the remark that it is still impossible to designate a specific type of discharge in which it is simplest to arrive at the optimum plasma-chemical reaction conditions described in this review. The fact that the best energy-efficiency indicators are currently obtained in medium-pressure microwave discharges does not prove that they are exceptional, especially when we consider powers exceeding 100 kW. It is even possible that each specific plasma-chemical process may require the construction of individual gas-discharge systems with characteristics that are optimal for this process alone. Nevertheless, it can be stated with certainty even now that nonequilibrium-plasma chemical processes stimulated by vibrational excitation of the reagents by plasma electrons are capable of productivities up to 10 m³ of product gas per hour from 1 cm³ of active plasma volume at energy efficiencies up to 80%. These indicators of the endoergic processes (first of all, the production of hydorgen and carbon monoxide), and especially their specific productivities, are far superior to those of alternative methods and can already be used today to solve various

important problems in atomic-hydrogen power engineering and metallurgy with the aid of nonequilibrium plasma chemistry.

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