SHIFT OF CHEMICAL EQUILIBRIUM IN A BINARY REACTING MIXTURE OF MOLECULAR GASES UNDER THE ACTION OF RESONANCE LASER RADIATION

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At the present time, great attention is being paid to the problem of the final state of molecular gas systems originating from a steady external effect. This is associated, first of all, with intensive investigations of the properties of molecular gas lasers and also laser initiation of chemical reactions and the isotope separation. The theoretical feasibility is shown in [1, 2] for effectively shifting the chemical equilibrium in "dissociation—three-particle recombination" reactions, initiated in a single-component gas by resonance laser radiation. The purpose of this paper is to analyze the shift of chemical equilibrium in a binary mixture of molecular gases as a function of the intensity and nature of the laser pumping. It is well known [3] that the equilibrium constant of a chemical reaction can be expressed in terms of the dissociation equilibrium constant of the molecules participating in the reaction This factor permits the problem to be reduced to calculation of the dissociation equilibrium constants.

§1. Let us consider a two-component system of molecules of types A and B. Suppose that radiation is effectively absorbed only by molecules of A. The effect of resonance laser radiation on this binary mixture will be written within the scope of the model which was used previously [4] for finding the distribution of molecules according to vibrational levels and the average margin of vibrational quanta. In order to analyze the shift of chemical equilibrium, the final (steady-state) stage of a "dissociation—three-particle recombination" reaction is the most interesting, in which recombination of the atoms—products of the reaction occurs. In this stage, for the reactions being considered,

$$A + M = 2a + M;\; B + M = 2b + M;\; M = A, B, a, b$$

the concentrations of products and reactants under equilibrium conditions (i.e., in the absence of pumping) are related by the law of mass action:

$$(N_a^{(0)})^2/N_A^{(0)} = \varkappa_A^{(0)},\; (N_b^{(0)})^2/N_B^{(0)} = \varkappa_B^{(0)},$$

where $N^{(0)}$ are the equilibrium concentration values; $\varkappa^{(0)}$ are chemical equilibrium constants (the suffixes A and B refer to molecules and suffixes a and b refer to atom-products).

The laser-radiation absorption shifts the chemical equilibrium; i.e., it changes the chemical equilibrium constants. In the steady state, the population of the last discrete vibrational level in the case being considered is found to be in detailed equilibrium with the number of atomic reaction products. Therefore, in accordance with the model given in [4], we shall have

$$P_{\mu d} x_\mu - P_{d\mu} N_a^2 = 0,\; P_{\nu d} y_\nu - P_{d\nu} N_b^2 = 0,$$

where x_μ and y_ν are the populations of the boundary levels μ and ν of molecules A and B; $P_{\mu d}$ and $P_{d\mu}$ ($P_{\nu d}$ and $P_{d\nu}$) are the number of collisions per unit time, respectively (for unit concentration of molecules and atoms), of molecules converted from the boundary level $\mu(\nu)$ to a continuous spectrum and conversely. Hence, the equations follow for the constants of the displaced chemical equilibrium:

$$\varkappa_A \equiv \frac{N_a^2}{N_A} = \frac{P_{\mu d}}{P_{d\mu}} \frac{x_\mu}{N_A},\; \varkappa_B \equiv \frac{N_b^2}{N_B} = \frac{P_{\nu d}}{P_{d\nu}} \frac{y_\nu}{N_B}. \tag{1.1}$$

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Taking into consideration that the probability ratios $P_{\mu d}/P_{d\mu}$ and $P_{\nu d}/P_{d\nu}$ are functions only of the temperature T, in the absence of pumping we obtain from Eq. (1.1)

$$\varkappa_A^{(0)} = \frac{P_{\mu d}}{P_{d\mu}} \frac{x_\mu^0}{N_A^0}, \ \varkappa_B^{(0)} = \frac{P_{\nu d}}{P_{d\nu}} \frac{y_\nu^{(0)}}{N_B^{(0)}}, \tag{1.2}$$

where

$$x_\mu^{(0)} = N_A^{(0)} (1 - e^{-\theta_A}) e^{-\mu\theta_A}, \ y_\nu^{(0)} = N_B^{(0)} (1 - e^{-\theta_B}) e^{-\nu\theta_B}$$

are the equilibrium (Boltzmann) populations of the boundary levels; $\theta_A = \hbar\omega_A/kT$ and $\theta_B = \hbar\omega_B/kT$; ω_A and ω_B are the frequencies of the oscillators A and B. In future, we shall assume the gas temperature to be constant, i.e., independent of the pumping intensity.

Taking Eq. (1.2) into account, relations (1.1) can be represented in the form

$$\varkappa_A = \varkappa_A^{(0)} \frac{x_\mu}{N_A} \left(\frac{x_\mu^{(0)}}{N_A^{(0)}}\right)^{-1}, \ \varkappa_B = \varkappa_B^{(0)} \frac{y_\nu}{N_B} \left(\frac{y_\nu^{(0)}}{N_B^{(0)}}\right)^{-1}. \tag{1.3}$$

It has been assumed in deriving Eq. (1.3) that isotopic-exchange reactions proceed more slowly than the dissociation reactions stimulated by the laser radiation. Substituting in Eq. (1.3) the expressions for x_μ and y_ν obtained in [4] in the case of multiquantum optical pumping, we shall have

$$\frac{\varkappa_A}{\varkappa_A^{(0)}} = F_k \xi_A^\mu \frac{e^{\mu\theta_A}}{1 - e^{-\theta_A}}, \ \frac{\varkappa_B}{\varkappa_B^{(0)}} = G \xi_B^\nu \frac{e^{\nu\theta_B}}{1 - e^{-\theta_B}}, \tag{1.4}$$

where

$$F_k = \frac{x_0}{N_A} \frac{1 + \frac{W_{k0}}{D_1} \frac{1}{\xi_A^k} \sum_{r=1}^{k} \frac{1}{r} \xi_A^{k-r}}{1 + \frac{W_{k0}}{D_1} \sum_{r=1}^{k} \frac{1}{r} \xi_A^{k-r}};$$

$$G = 1 \Big/ \sum_{n=0}^{\nu} \xi_B^n; \ \xi_A = C_1/D_1;$$

$$C_1 = P_{10}(A) e^{-\theta_A} + N_A Q_{10}^{01}(AA) \alpha_A + N_B Q_{10}^{01}(AB) e^{\Delta} \alpha_B;$$

$$D_1 = P_{10}(A) + N_A Q_{10}^{01}(AA)(1 + \alpha_A) + N_B Q_{10}^{01}(AB)(1 + \alpha_B);$$

$$\xi_B = C_2/D_2;$$

$$C_2 = P_{10}(B) e^{-\theta_B} + N_B Q_{10}^{01}(BB) \alpha_B + N_A Q_{10}^{01}(AB) \alpha_A;$$

$$D_2 = P_{10}(B) + N_B Q_{10}^{01}(BB)(1 + \alpha_B) + N_A Q_{10}^{01}(AB) e^{\Delta} (1 + \alpha_A);$$

$$x_0 = N_A \left(1 + \frac{W_{k0}}{D_1} \sum_{r=1}^{k} \frac{1}{r} \xi^{k-r}\right) \left\{\sum_{n=0}^{\mu} \xi_A^n + \frac{W_{k0}}{D_1} \left[\sum_{r=1}^{k} \frac{1}{r} \xi_A^{k-r} + \right.\right.$$
$$\left.\left. + (1 - \xi_A^k) \sum_{n=1}^{k} \sum_{r=1}^{n} \frac{1}{r} \xi_A^{n-r} + \sum_{n=h+1}^{\mu} \sum_{r=1}^{k} \frac{1}{r} \xi_A^{n-r} + \sum_{n=1}^{k} \sum_{r=1}^{k} \frac{1}{r} \xi_A^{n+k-r}\right]\right\}^{-1}.$$

Here $W_{k0} = W_{0k}$ are the probabilities of multiquantum vibrational transitions $0 \rightleftarrows k$, created by laser pumping; $P_{10}(A)$ and $P_{10}(B)$ are the probabilities (sec^{-1}) of V—T processes, so that $P_{10}(A) = \sum_\beta N_\beta P_{10}(A\beta)$, $P_{10}(B) = \sum_\beta N_\beta P_{10}(B\beta)$, and N_β is the number of particles of type β in unit volume (subscripts β = a and b refer to the concentration of atoms—products and subscripts β = A and B refer to the concentration of molecules of types A and B); $P_{10}(AA)$, $Q_{10}^{01}(AA)$, and $Q_{10}^{01}(AB)$ are the probabilities of single-quantum processes of vibrational—translational energy exchange (V—T process), vibrational—vibrational exchange of energy within (V—V process) and between (V—V' processes) components, respectively, referred to unit time and unit concentration of collision partners; $\alpha_A = \sum_{n=0}^{\mu} n x_n / N_A$ and $\alpha_B = \sum_{n=0}^{\nu} n y_n / N_B$ are the number of vibrational quanta of molecules A and B (expressions for α_A and α_B are obtained in [4]).

In the limiting cases ξ_A, $\xi_B << 1$ and ξ_A, $\xi_B \lesssim 1$, the functions F_k and G assume the simple form

$$F_k = \frac{1 + \frac{W_{k0}}{D_1}\frac{1}{k}\frac{1}{\xi_A^k}}{1 + \frac{W_{k0}}{D_1}\left(\frac{1}{k} + \sum_{r=1}^{k}\frac{1}{r}\right)},\ G = 1,\ \xi_A,\ \xi_B \ll 1;$$
$$F_k(1-\xi_A)\frac{1 + \frac{W_{k0}}{D_1}\frac{1}{\xi_A^k}\sum_{r=1}^{k}\frac{1}{r}}{1 + \frac{W_{k0}}{D_1}\xi_A\sum_{r=1}^{k}\frac{1}{r}},\ G = 1 - \xi_B,\ \xi_A,\ \xi_B \lesssim 1. \qquad (1.5)$$

In special cases, when N_A, $N_B >> N_a$, N_b (i.e., $N_A \simeq N_A^0$, $N_B \approx N_B^0$) and N_a, $N_b >> N_A$, N_B (i.e., $N_a \approx 2N_A^0$, $N_b \simeq 2N_B^0$), the functions F_k and G are independent of the concentrations N_A, N_B, N_a, and N_b and, consequently, Eq. (1.4) gives the explicit form of the dependence of the displaced chemical equilibrium constants on the optical pumping probability. In the cases mentioned, the explicit expressions for the concentrations can be obtained also from Eq. (1.1)

$$N_A,\ N_B \gg N_a,\ N_b : N_a = \sqrt{N_A^0 \varkappa_A},\ N_b = \sqrt{N_B^0 \varkappa_B};$$
$$N_a,\ N_b \gg N_A,\ N_B : N_A = 4(N_A^0)^2/\varkappa_A,\ N_B = 4(N_B^0)^2/\varkappa_B. \qquad (1.6)$$

Thus, it can be seen from the formulas derived above that the shift of the chemical equilibrium is due to the deviation of the population of the boundary vibrational level from the equilibrium value. This is due to the presence of optical pumping, which leads to distortion of the Boltzmann distribution at the levels $0 \leq n \leq k$ of molcules of component A and an increase of the vibrational temperatures of both components.

Figure 1 shows the dependence of $\varkappa_A/\varkappa_A^{(0)}$ on the dimensionless probability of optical pumping $W_{k0}/N_A^0Q_{10}^{01}(AA)$, calculated by formulas (1.4) and (1.5) (curve 1 represents a single-component system, curves 2-4 are plotted for values of $N_B^0/N_A^0 = 1$, 10^2, and 10^4; $k = 1$). The following values of the molecular parameters have been used in the calculations: $P_{10}(AA) \approx P_{10}(BB) \approx P_{10}(AB)$; $Q_{10}^{01}(AA) \approx Q_{10}^{01}(BB) \approx Q_{10}^{01}(AB)$; $Q_{10}^{01}(AA)/P_{10}(AA) = 10^5$; $P_{10}(Aa) \approx P_{10}(Ab) \approx P_{10}(Ba)$; $Q_{10}^{01}(AA)/P_{10}(Aa) = 2 \cdot 10^3$; $\mu = \nu = 25$; $\hbar\omega_A = 2359.6\ cm^{-1}$; $\Delta = -0.1$; $T = 300°K$. These molecular parameters correspond to mixtures of isotope molecules $^{14}N^{14}N$ (type A) and $^{14}N^{15}N$ (type B). It can be seen from Fig. 1 that with increasing pumping intensity, the quantity $\varkappa_A/\varkappa_A^{(0)}$ increases steeply and, for intensities which ensure fulfillment of the condition $W_{k0} \geq N_A^0Q_{10}^{01}(AA)(1 + \alpha_A) + N_B^0Q_{10}^{01}(AB)(1 + \alpha_B)$, reaches saturation.

Using the above molecular parameters, let us estimate the maximum permissible concentrations of atoms-products. In the saturation mode, $\varkappa_A/\varkappa_A^{(0)} \approx 10^{11}\ cm^{-3}$. When $N_A^0 \approx 10^{17}\ cm^{-3}$, $T \approx 300°K$, and $\varkappa_A^{(0)} \approx 7 \cdot 10^{-9}\ cm^{-3}$ [5], it follows from Eq. (1.6) that the maximum concentration of atoms $N_a \approx 10^{15}\ cm^{-3}$. We note that in the absence of laser radiation (other conditions being equal) $N_a \approx 10^{-41}\ cm^{-3}$. Thus, the estimate carried out confirms the possibility of obtaining quite high concentrations of free atoms by the steady selective excitation of the molecular vibrations of atoms.

§2. The possibility shown above of effectively shifting the chemical equilibrium in a binary mixture permits the interesting problem of isotope separation in a steady-state "dissociation—three-particle recombination" reaction mode to be analyzed. The quantity

$$\gamma = \frac{\varkappa_A/\varkappa_A^{(0)}}{\varkappa_B/\varkappa_B^{(0)}} - 1, \qquad (2.1)$$

which is related to the conventional separation factor by products [6]

$$\gamma^* = \frac{N_a/N_b}{N_A^0/N_B^0} - 1$$

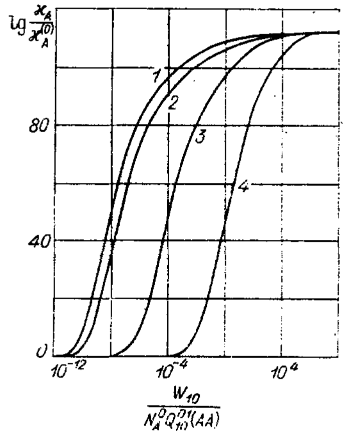

Fig. 1

by the relation

$$\gamma^* = \sqrt{(\gamma+1)\frac{N_B^0}{N_A^0}e^{\mu\Delta}},$$

where $\Delta = \theta_B - \theta_A$, can serve as a measure of the separation efficiency in the given case.

Let us analyze the behavior of γ in the limiting case N_A, $N_B >> N_a$, N_b. In this case, expression (2.1) assumes the form

$$\gamma = F_k\left(\frac{\xi_A}{\xi_B}\right)^{\mu} e^{-\mu\Delta} - 1, \tag{2.2}$$

where F_k is given by expression (1.5). It follows from Eq. (1.5) and (2.2) that for $W_{k0} = 0$, $\gamma = 0$. The dependence of γ on W_{k0} is determined mainly by the function F_k (the quantities ξ_A and ξ_B are of one order). With $W_{k0}/D_1 >> 1$, the function F_k assumes a constant value

$$F_k = \frac{1}{1 + k\sum_{r=1}^{k}\frac{1}{r}}\frac{1}{\xi_A^k}, \quad \xi_A \ll 1;$$

$$F_k = \frac{1-\xi_A}{\xi_A}\frac{1}{\xi_A^k}, \quad \xi_A \lesssim 1,$$

and, consequently, $\gamma > 0$. It can be seen from Eq. (1.5) that, in regions of weak pumpings ($W_{k0}/D_1 << 1$), the function F_k has a maximum for $k > 1$.

By way of example, Fig. 2a–c shows the dependence of γ on the intensity of the laser radiation, calculated by formulas (1.5) and (2.2) [a) curves 1 and 2 (left-hand scale) and 3 (right-hand scale) correspond to k = 1, 2, 3 and $N_B^0/N_A^0 = 10^2$; b) the solid curve corresponds to $N_B^0/N_A^0 = 10^{-4}$, the dashed curve to $N_B^0/N_A^0 = 10^2$, the dot-and-dashed curve to $N_B^0/N_A^0 = 10^3$ (plotted on the scale 1:10), the dashed curve with two points to $N_B^0/N_A^0 = 10^4$ (plotted on the scale 1 : 100), all curves correspond to $k = 2$; c) curves 1–3 are plotted for values of $N_B^0/N_A^0 = 1$, 10^4, 10^6 and $k = 1$]. It can be seen from Fig. 2a and b that the behavior of γ is of a nonmonotonic nature: When $W_{k0}/D_1 <<1$, starting from a certain pumping value, γ increases steeply from zero, reaches a maximum, and then falls. Hence, it follows that, in contrast from the conclusion of [7], in principle it is possible to achieve appreciable values of γ in the steady-state cycle.

The physical explanation consists in the following. With increase of W_{k0} from zero, the Boltzmann distribution function of molecules of type A at levels $0 \leq n \leq k$ is distorted in consequence of the transfer of molecules from the level n = 0 to the level n = k by the laser radiation. The distortion of the distribution leads to an increase of the population of levels n > k and, consequently, to a reduction of the contribution of the distortion of the distribution function to the relative population of the boundary level x_μ/N_A. In proportion with the further increase of W_{k0}, γ again increases and reaches the saturation mode. The increase on this section is due to the preferential heating of type A oscillators.

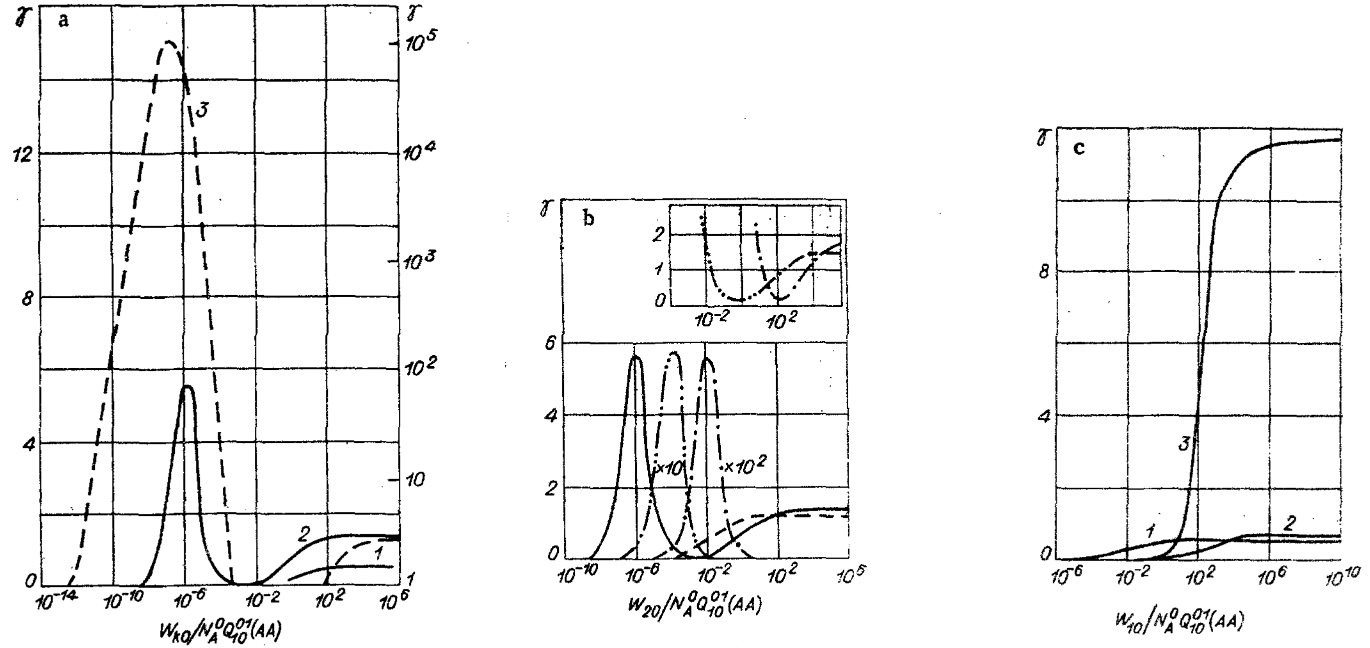

Fig. 2

It follows also from Fig. 2a and b that the quantity γ depends significantly on the nature of the pumping (one-, two-, or three-quantum pumping): With increase of k, the distortion of the distribution function and, consequently, also the value of γ, is increased.

The effect of the ratio of the concentrations N_B^0/N_A^0 on the magnitude and position of the curve maxima is shown in Fig. 2b and c. Dissociation and transference of vibrational energy from system A to system B, which is intensified with increase of N_B^0/N_A^0, causes a shift to the right of the curves. It can also be seen from the figures that dilution of the gas A with gas B permits the laser radiation to aim for a strong distortion of the Boltzmann distribution function (consequently, the achievement of large values of γ) even with $k = 1$.

Thus, as the calculations carried out have shown, the effect of optical pumping leads to a considerable displacement of the chemical equilibrium in the two-component system considered and, in principle, admits the possibility of separating isotopes in the steady-state stage of a "dissociation—three-particle recombination" reaction.

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LITERATURE CITED

1. B. F. Gordiets, A. I. Osipov, V. Ya. Panchenko, and R. V. Khokhlov, "Dissociation of polyatomic molecules in a laser radiation field," in: Thesis of Reports Presented at the Seventh All-Union Conference on Coherent and Nonlinear Optics [in Russian], MGU, Moscow (1974).
2. B. F. Gordiets, A. I. Osipov, and V. Ya. Panchenko, "Kinetics of the 'dissociation—three-particle recombination' process, initiated by infrared laser radiation," in: Thesis of Reports Presented at the Second All-Union Congress on Photochemistry [in Russian], MGU, Moscow (1974); "Shift of chemical equilibrium in the field of resonant infrared laser radiation," Zh. Prikl. Mekh. Tekh. Fiz., No. 1, 10 (1976).
3. V. N. Kondrat'ev and E. E. Nikitin, Kinetics and Mechanism of Gas-Phase Reactions [in Russian], Nauka, Moscow (1975).
4. T. Z. Kalanov, A. P. Osipov, and V. Ya. Panchenko, "Distribution of vibrational energy in a binary reacting mixture of molecular gases in the field of resonant laser radiation," Zh. Prikl. Mekh. Tekh. Fiz., No. 4 (1977).
5. R. Kubo, Statistical Mechanics, American Elsevier (1965).
6. S. F. Peterson and R. G. Wymer, Chemistry in Nuclear Technology, Addison-Wesley (1968).
7. L. P. Kudrin and Yu. V. Mikhailova, "Kinetics of excitation of molecular gases by laser radiation," Zh. Éksp. Teor. Fiz., 68, No. 6, 2095 (1975).