SOVIET PHYSICS JETP VOLUME 28, NUMBER 4 APRIL, 1969

A CHEMICAL LASER BASED ON BRANCHED REACTIONS

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Submitted April 25, 1968

Zh. Eksp. Teor. Fiz. 55, 1423—1429 (October, 1968)

Branched chain reactions are proposed as the basis of a chemical laser, the radiation energy of which depends weakly on the pumping energy. Conditions are derived which must be satisfied by the parameters of the reacting mixture in order to obtain population inversion.

THE attempts made over the course of many years to create chemical lasers[1-7] have resulted in a number of experimental successes.[8-10] The experimental results obtained in[8-11] are a direct proof of the occurrence of inversion in the process of certain chemical reactions. However, in the lasers described in these papers an expenditure of energy considerably in excess of the output energy is required to initiate the chemical reaction. Hence the experimental successes achieved can scarcely be regarded as the culmination of the work on chemical lasers. Rather, they form the experimental basis which creates a real foundation for the discussion of means of realizing chemical lasers whose energy output in the form of useful radiation exceed the expended energy.

It is obvious that the way to such a laser is through a self-maintaining reaction. Among these (combustion, explosion, etc.), the most promising seem to be chain reactions, the importance of which for lasers was indicated already in[2,3]. Interest in these reactions is also engendered by the experimental results that have been obtained: in[8,9] population inversion and generation were obtained in hydrogen-halogen reactions, which belong to this class. Hence the following analysis is devoted to just these chain (simple and branched) reactions. For simplicity, we shall consider certain idealized schemes, having in mind, however, hydrogen-halogen reactions.

The simple chain reaction. Consider the kinetics of the following chain process:

initiation of a chemical reaction:

$$A_2 + Q = 2A; \tag{1a}$$

an elementary act of reaction, not leading to inversion:

$$A + B_2 = AB_0 + B; \tag{1b}$$

an act of reaction leading to inversion:

$$B + A_2 = AB^+ + A; \tag{1c}$$

a relaxation process:

$$AB^+ + M = AB + M. \tag{1d}$$

Here A_2 and B_2 are the initial reactants, AB^+ is a molecule in the upper working level, AB is a molecule in the lower working level, AB_0 is a molecule in the ground state, Q is the energy supplied to the system for the formation of chemically active centers, and M is any of the reactants. The energy scheme of the reaction is represented in Fig. 1. This scheme is close to that for the reaction of H_2 with Cl_2.[9]

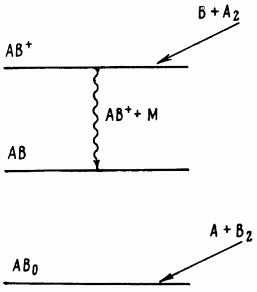

FIG. 1

The rate equations describing this process have the form

$$\begin{aligned}\frac{d}{dt}[AB^+] &= k^*[A_2][B] - k_1[M][AB^+],\\ \frac{d}{dt}[AB] &= k_1[M][AB^+],\\ \frac{d}{dt}[A] &= k^*[A_2][B] - k[B_2][A] + k_0[A_2],\\ \frac{d}{dt}[B] &= -k^*[A_2][B] + k[B_2][A],\end{aligned} \tag{2}$$

where k^*, k, k_1, k_0 are respectively the rate constants of the reactions (1c), (1b), (1d), and (1a); for initiation of the reaction by light the quantity k_0 is proportional to the photon density and the photodissociation cross section. The symbol [ ] signifies the concentration of a reagent. Actually, the system (2) should be augmented by equations for the change in the concentrations $[A_2]$ and $[B_2]$. However, we shall be interested in the linear approximation, assuming $[A_2]$ and $[B_2]$ to be invariable. For convenience, we introduce the dimensionless variables

$$x^* = \frac{[AB^+]}{[B_2]_0}, \quad x = \frac{[AB]}{[B_2]_0},$$
$$u = \frac{[A]}{[B_2]_0}, \quad v = \frac{[B]}{[B_2]_0},$$
$$\tau = k^*[B_2]_0 t, \quad \sigma = \frac{k[A_2]}{k^*[B_2]_0},$$
$$\sigma_1 = \frac{k_1[M]}{k^*[B_2]_0}, \quad \gamma = \frac{k_0[A_2]}{k^*[B_2]_0^2},$$

where $[B_2]_0$ is the (initial) concentration of molecules B_2. Then (2) is rewritten in the form

$$\frac{dx^*}{d\tau} = v - \sigma_1 x^*, \quad \frac{dx}{d\tau} = \sigma_1 x^*,$$
$$\frac{du}{d\tau} = v - \sigma u + \gamma, \quad \frac{dv}{d\tau} = -v + \sigma u. \tag{3}$$

The solution to the system (3) for initial conditions $x^* = x = u = v = 0$ at $\tau = 0$ has the form

$$x^* = e^{-\sigma_1\tau}\int_0^\tau v(\tau')e^{\sigma_1\tau'}d\tau', \quad x = \sigma_1\int_0^\tau x^*(\tau')d\tau',$$

$$v(\tau) = \sigma e^{-(1+\sigma)\tau}\int_0^\tau d\tau' e^{(1+\sigma)\tau'}\int_0^{\tau'} \gamma(\tau'')d\tau''. \tag{4}$$

We shall assume that excitation is effected by a short pulse, the length of which τ_0 is considerably less than the relaxation time. Then the maximum value of the population inversion for $1 + \sigma \gg \sigma_1$ is

$$(x^* - x)_{max} \approx (1 - \ln 2)\frac{\sigma}{1+\sigma}\frac{1}{\sigma_1}\int_0^{\tau_0}\gamma(\tau')d\tau'. \tag{5}$$

The maximum number of active particles depends on the ratio of the reaction and relaxation rates. The quantity $\sigma/(1 + \sigma)\sigma_1$ determines the effective length of the chain that gives a contribution to the population inversion.

In (3) there is no assumption about breaking of the chain due to chemical processes, and the finiteness of the effective chain length is determined by the relaxation time. But if the chain length ν due to chemical processes is less than $\sigma/(1 + \sigma)\sigma_1 = \nu_{\text{eff}}$, then

$$(x^* - x)_{max} \approx \nu\int_0^{\tau_0}\gamma(\tau')d\tau'. \tag{6}$$

The integral appearing in (5) is proportional to the absorbed number of pump quanta. Hence even for a long effective chain length the output power of a chemical laser will be determined by the pump intensity. And if one considers the inevitable energy losses in the ratio of an emitted to an absorbed quantum, in the ratio of the total spectrum of the pumping source to the absorbed spectrum, etc., then the dependence of the output power on the pump intensity becomes extremely significant.

The branched reaction. For such reactions it has been shown[12] that the rate grows exponentially with time. This gives grounds for supposing that the number of active particles obtained in the final stage is independent of the energy initiating the reaction. However, they have been investigated only from the viewpoint of chemical kinetics. The necessity of obtaining a population inversion imposes, as will be evident from the following, a number of limitations on the rate of the elementary acts of a branched chemical reaction.

We assume the following branching scheme:

$$AB^+ + RA = AB + R + A, \tag{7}$$

where RA is some additional reagent that dissociates upon collision with an excited molecule AB^+. Then to the Eqs. (3) we add a term corresponding to the branching process, so that

$$\frac{dx^*}{d\tau} = v - (\sigma_1 + \sigma_2)x^*, \quad \frac{dx}{d\tau} = (\sigma_1 + \sigma_2)x^*,$$

$$\frac{du}{d\tau} = v - \sigma u + \sigma_2 x^* + \gamma, \quad \frac{dv}{d\tau} = -v + \sigma u, \tag{8}$$

where $\sigma_2 = k_2[RA]/k^*[B_2]$, and k_2 is the rate constant of the process (7). The system of equations has three linearly independent solutions that vary exponentially with time. Two of these decay and one grows with time. After a certain interval of time, this growing exponential will be dominant, so that the solution of (8) may be written

$$x^* = Ae^{s\tau}, \quad x = \frac{\sigma_1 + \sigma_2}{s}Ae^{s\tau}, \tag{9}$$

where A is a constant that depends on the intensity of illumination, and s is the positive root of the equation

$$s^3 + s^2(1 + \sigma + \sigma_1 + \sigma_2) + s(1 + \sigma)(\sigma_1 + \sigma_2) - \sigma\sigma_2 = 0. \tag{10}$$

The condition of exponential growth of the inverted population leads to the inequality

$$s > \sigma_1 + \sigma_2. \tag{11}$$

If the rate of branching is small compared to the process (1c), then $s = \sigma\sigma_2/\sigma_1$, so that the condition (11) takes the form

$$\frac{\sigma}{1+\sigma}\sigma_2 > (\sigma_1 + \sigma_2)^2. \tag{12}$$

The relation (12) is modified if it is assumed that as a result of dissociation of a molecule RA due to collision with AB^+ the latter falls into a "non-working" level "0" (see Fig. 1), i.e., the reaction goes according to

$$AB^+ + RA = R + A + AB_0.$$

Then instead of (12) we have

$$\frac{\sigma}{1+\sigma}\sigma_2 > \sigma_1(\sigma_1 + \sigma_2). \tag{13}$$

The inequalities (12) and (13) in the limiting case of high rates of branching ($\sigma_2 \gg \sigma_1$) have a different physical meaning:

$$\frac{\sigma}{1+\sigma} > \sigma_2, \tag{12a}$$

$$\frac{\sigma}{1+\sigma} > \sigma_1. \tag{13a}$$

At the same time both relations in the case of small branching rates give

$$\frac{\sigma}{1+\sigma}\sigma_2 > \sigma_1^2. \tag{14}$$

Conditions (12) and (13) superpose a limitation on the partial densities of the reactants and the temperature of the reacting mixture. Actually, the rate constants of the reactions may be represented in the form[12]

$$k = r\varphi(T), \tag{15}$$

where r is a constant quantity depending on the nature of the interacting molecules; $\varphi(T)$ is a function of temperature, usually of the form

$$\varphi(T) \sim e^{-\Delta E/kT}, \tag{16}$$

where ΔE is the activation energy of the process.

For illustration, we consider the simple case of low branching rates ($\sigma_2 \ll \sigma_1$), and also set $\sigma \ll 1$. Then (14), with (15), can be written

$$\frac{(1 + \eta + \xi)^2}{\eta\xi} < \frac{rr_2}{r_1^2}F(T), \tag{17}$$

where ξ is the ratio of densities $[RA]/[B_2]$, and $\eta = [A_2]/[B_2]$, F(T) is some function of temperature. Since physically $\eta > 0$ and $\xi > 0$, then from (17) must come the requirement

$$\frac{rr_2}{r_1^2}F(T) \geqslant \frac{1+\eta}{\eta}, \tag{18}$$

for which there exists a region of values of ξ that satisfy the inequality (17):

$$\xi_- < \xi < \xi_+, \tag{19}$$

where ξ_+ and ξ_- are the roots of the quadratic equation

$$\xi^2 + 2\left(1+\eta-\eta\frac{rr_2}{2r_1^2}F(T)\right)\xi + (1+\eta)^2 = 0. \tag{20}$$

Thus, here we have a certain equivalent to the "ignition peninsula" in branched chain reactions.[12] We should like to emphasize the principal distinction of our "peninsula": this "peninsula" is associated with obtaining an inverted population and departure from it cannot disrupt the vigorous course of a reaction; however, it will go on without producing inversion.

Analogous conclusions can be drawn about η, since both ξ and η enter into Eq. (17) in a completely symmetrical way. If the branching is effected by reactant B_2:

$$AB^+ + B_2 = 2B + AB_0,$$

then the "peninsula" is retained:

$$\eta_- < \eta < \eta_+, \tag{21}$$

η_+, η_- are the roots of the equation

$$\eta^2 + \left[2 - \frac{rr_2}{r_1^2}F(T)\right]\eta + 1 = 0, \tag{22}$$

where we must have

$$\frac{rr_2}{r_1^2}F(T) \geqslant 4. \tag{23}$$

And if branching of the reaction occurs by way of dissociation of A_2 molecules:

$$AB^+ + A_2 = 2A + AB_0,$$

then it is necessary that

$$\frac{rr_2}{r_1^2}F(T) > 1 \tag{24}$$

and

$$\eta > \left(\sqrt{\frac{rr_2}{r_1^2}F(T)} - 1\right)^{-1}. \tag{25}$$

Fulfillment of the conditions enumerated above guarantee the exponential growth of the inverted population with time in the initial stage of the reaction. The expenditure of the initial reactants, obviously, will lead to a limitation on the growth of inversion. In order to follow the entire process of change of $x^* - x$ with time it is necessary to add to the system (8) equations that describe the change of concentration of A_2, B_2, and RA with time. The parameters σ_i in this case also become variable, since we must deal with a nonlinear system of equations.

Up until now we have not considered the possibility of populating the lower of the working levels in the course of the reaction $A_2 + B$. However, such population occurs in real systems. It is not difficult to generalize the results obtained to cover this case also. All the considerations and calculations we set forth in obtaining the inequality (11) remain in force, however, the inequality itself becomes the relation

$$s > \sigma_1 + \sigma_2 + \frac{\sigma\sigma_2}{s(s+1+\sigma)}\,\frac{1-\alpha}{\alpha}, \tag{26}$$

where α is the probability of the reaction $A_2 + B = AB^+ + A$, and $1 - \alpha$ is the probability of the channel $A_2 + B = AB + A$. Obviously, to obtain inversion we must have $\alpha > 0.5$.

With all the assumptions that led to (17), the inequality (26) takes the form $\sigma\sigma_2/\sigma_1^2 > 1/\alpha$. It is seen that Eqs. (17)–(25) remain in force also for the case of population of the lower level if we replace F(T) in them by $F(T)/\alpha$.

We have set up a system of equations in which, together with the decrease of concentrations [A], [B], and [RA], the possible reactions

$$B + AB^+ = A + B_2,$$
$$B + AB = A + B_2.$$

were also taken into account. The constants of all reactions were to a certain extent selected arbitrarily. However, in their selection, we had in mind the reaction of hydrogen with chlorine.[12] The dependence on time of the exciting light pulse was taken in the form

$$\gamma(t) = \gamma n\frac{e^{-\gamma\tau}}{(1+e^{-\gamma\tau})^2},$$

which qualitatively reflects the character of the light flux from a pulsed lamp.

Figure 2 shows the dependence $x^*(\tau) - x(\tau)$ for different intensities of light initiating the reaction. The kinetic parameters used to obtain these curves are: $\gamma = 10^{-4}$; $\alpha_0 = k/k^* = 1$; $\alpha_1' = k_1'/k^* = 0.01$; $\alpha_1 = k_1/k^* = 0.001$; $\alpha_2 = k_2/k^* = 0.001$; $\alpha_3 = k_3/k^* = 0.001$, where k_1' is the rate constant for the establishment of thermal equilibrium due to collisions of AB^+ with AB^+, AB and AB_0; k_1 is the same as k_1' for collisions with other particles; k_3 is the rate constant of the reactions $AB^+ + B = A + B_2$ and $AB + B = A + B_2$. Figure 2 clearly demonstrates the independence of the maximum inversion on the intensity of initiation of reaction, which could be expected from the exponential growth of inversion at the initial moments of time.

The fact that a branched reaction goes independently of the degree of initiation creates a difficulty in its experimental realization, since the time of the reaction may turn out to be less than the time of preparing the initial mixture of reagents. Here inhibitors may be of use; these are substances the addition of which even in small quantities to the reacting mixture strongly slows down the reaction.[12] After preparation of the mixture

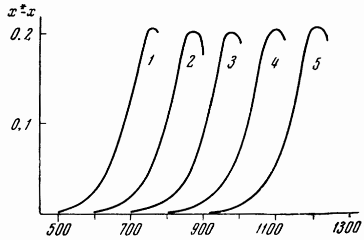

FIG. 2. The function $x^*(\tau) - x(\tau)$ for different intensities of the light initiating the reaction. Initial conditions: for $\tau = 0$, $[A_2] = [B_2] = [RA] = [A] = [B] = [AB^+] = [AB] = 0$. Values of n for curve $1-10^{-5}$; $2-10^{-6}$; $3-10^{-7}$; $4-10^{-8}$; $5-10^{-9}$.

the inhibitor can be disposed of by a sufficiently strong initiation of the reaction, and as a result of the subsequent rapid development of the branched reaction in the reacting mixture a ''pulse'' of inverted population arises, which can be used for generation. In such a mixture the formation of a ''pulse'' of inverted population recalls in its mechanism the formation of a pulse of light in a laser with a clarifying filter.

We have here analyzed the simplest scheme of chain and branched reactions. In real systems not all the energy developed in the reaction process goes into radiation and the reacting mixture becomes heated. Heating of the mixture will lead to a change in the rates of the individual reactions and inevitably to a significant alteration of the kinetics of the reaction as a whole. However, this does not change the relations obtained above, which are valid for the initial stage of the reaction. It makes sense, however, to carry out a complete analysis of the kinetics with account taken of the heat balance for specific compositions of the reacting mixture.

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[1] J. C. Polanyi, J. Chem. Phys. **34**, 347 (1961).

[2] A. N. Oraevskiĭ, Zh. Eksp. Teor. Fiz. **45**, 177 (1963) [Sov. Phys.-JETP **18**, 126 (1964)].

[3] V. L. Tal'roze, Kinetika i kataliz **5**, 11 (1964).

[4] J. C. Polanyi, Chemical Lasers, Opt. Soc. Am., Washington, DC, 1965, p. 109.

[5] H. P. Broida, Chemical Lasers, Opt. Soc. Am., Washington, DC, 1965, p. 105.

[6] K. E. Shuler, T. Carrington, and I. C. Light, Chemical Lasers, Opt. Soc. Am., Washington, DC, 1965, p. 81.

[7] M. Hertzberg, Symposium on Optical Masers, Brooklyn, Interscience, New York, 1963.

[8] J. V. V. Kasper and G. C. Pimentel, Phys. Rev. Letters **14**, 352 (1965).

[9] K. G. Anlauf, D. H. Maylotte, P. D. Pacey, and J. C. Polanyi, Phys. Letters **24A**, 208 (1967).

[10] T. F. Deutsch, Appl. Phys. Letters **10**, 234 (1967).

[11] K. L. Kompa and G. C. Pimentel, J. Chem. Phys. **47**, 857 (1967).

[12] V. N. Kondrat'ev, Kinetika khimicheskikh gazovykh reaktsiĭ (Kinetics of Chemical Gas Reactions), AN SSSR, 1958 (Engl. transl., Addison-Wesley, Reading, Mass., 1964).

Translated by L. M. Matarrese
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