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EXOTHERMIC GAS-PHASE REACTORS AS THE CAUSE OF MULTITEMPERATURE  
FLOWS OF POLYATOMIC GASES

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A multitemperature flow is usually understood as a flow of a polyatomic gas with different temperatures for the translational and vibrational degrees of freedom [1-3]. There can be differences in translational temperature in components of a mixture, which is one of the consequences of marked differences in molecular mass. The most familiar example of this kind is an ionized gas in an external electric or electromagnetic field [4, 5]. An example has been considered [6] of a multitemperature state for the translational degrees of freedom due to an endothermic reaction in a one-component light gas, which is in a thermostat composed of the heavy component that is neutral in relation to the reaction. The state of the diluent is not perturbed by the reaction, which is examined for times such that one can neglect the reverse reaction. A similar treatment is found in [7-10], where various cases of nonequilibrium velocity distributions were considered for components of a chemically reacting mixture.

A characteristic feature of an exothermic reaction in a mixture with substantial differences between the masses of the molecules is that the energy released by an elementary act is borne off almost completely by the lighter product. There is only slow energy exchange in collisions between particles differing considerably in mass, so the locally equilibrium energy distribution for the translational degrees of freedom of each of the components may occur before complete equilibrium. This situation is described by the equations of multitemperature gasdynamics, which are derived here.

1. Consider the collision of molecules  $A_i$  and  $A_j$ , which leads to the reaction  $A_i + A_j \rightarrow A_k + A_l$ , in which the energy  $E_{ij}^{kl} \equiv E_i + E_j - E_k - E_l \equiv Q$  is released and is converted to translational degrees of freedom of the molecules, where  $E_i$  is the internal energy of molecule  $A_i$ . The speeds of  $A_k$  and  $A_l$ , which are produced by the collision, are related to the speeds of  $A_i$  and  $A_j$  by the collision relations

$$\begin{aligned} c_k &= G_{ij} + (2m_i R / m_0 m_k)^{1/2} e_f, \quad c_l = G_{ij} - (2m_j R / m_0 m_l)^{1/2} e_f, \\ G_{ij} &= \mu_i c_i + \mu_j c_j, \quad R = Q + \mu_{ij} g_{ij}^2 / 2, \quad g_{ij} = |g_{ij}| = |c_i - c_j|, \end{aligned} \quad (1.1)$$

where  $m_i$  is the mass of molecule  $i$ ,  $m_0 = m_i + m_j = m_k + m_l$ ,  $\mu_i = m_i m_0^{-1}$ ,  $\mu_{ij} = m_i m_j$ ,  $e_f = g_{kl} g_{kl}^{-1}$ . The mean energy of motion of the  $A_l$  produced in the reaction of  $A_i$  and  $A_j$  is defined by the following expressions, where the latter have Maxwellian distributions  $f_{i0} = n_i (h_i / \pi)^{3/2} \exp(-h_i c_i^2)$ , where  $h_i = m_i / 2kT$  ( $n_i$  and  $T$  are the numerical density of the  $i$  molecules and the gas temperature, while  $k$  is Boltzmann's constant):

$$\int f_{i0} f_{j0} g_{ij} d\sigma_{ij}^{kl} dc_i dc_j \left\langle \frac{m_l c_l^2}{2} \right\rangle = \int f_{i0} f_{j0} \frac{m_l c_l^2}{2} g_{ij} d\sigma_{ij}^{kl} dc_i dc_j = \int f_{i0} f_{j0} \left( \frac{m_l G_{ij}^2}{2} + \frac{m_k \mu_{ij} g_{ij}^2}{m_0} + \frac{m_k}{m_0} Q \right) g_{ij} d\sigma_{ij}^{kl} dG_{ij} dg_{ij}, \quad (1.2)$$

where  $\sigma_{ij}^{kl}$  is the cross section for  $A_i + A_j \rightarrow A_k + A_l$ , which here and subsequently are assumed to be a function of  $g_{ij}$  and the central parameter of the collision. We neglect any possible dependence of  $\sigma_{ij}^{kl}$  on the orientation of the colliding molecules.

We see from (1.2) that for  $m_l \gg m_k$  the heavier molecule  $A_l$  carried off only a small part of  $Q$ , which is transferred mainly to  $A_k$ . If the characteristic time of the flow or process  $\tau_*$  satisfies  $\tau_R \leq \tau_* \leq \tau_\Delta$ , where  $\tau_R$  and  $\tau_\Delta$  are the times of chemical reaction and the establishment of equilibrium in temperature between the heavy and light components, then the description should be constructed on a multitemperature basis.

The generalized Chapman-Enskog method proposed in [11-13] and developed in [14-18] may be used to derive the gasdynamic equations. In particular, in [18] the method was applied to a multiveLOCITY multitemperature flow. However, the mechanism responsible for the multitemperature state was not specified, and the forms of the reaction and exchange terms appearing in the equations were not defined.

We have used a form of the method similar to that represented in [11-13, 16] to derive the gasdynamic equations. The differences lie in the details, which reflect the specific features of the problem, and therefore they are not specially mentioned. Determination of the particular form of some of the exchange terms in the transport equations involves a model for inelastic collision based on the assumption that the direction of the relative velocity of the molecules resulting from the collision is unrelated to the direction of the relative velocity of the colliding molecules. It is assumed that conditions in the mixture are such that the difference in the mean-mass velocities of the components is unimportant (e.g., comparable concentrations).

The equations of the zero (Euler) approximation in the Knudsen number are constructed in this way:

$$\begin{aligned} \frac{Dn_i}{Dt} + n_i \frac{\partial u_\alpha}{\partial x_\alpha} &= R_i^{(0)}, \quad \rho \frac{Du_\alpha}{Dt} = - \frac{\partial p}{\partial x_\alpha}, \\ \frac{3}{2} kn_i \frac{DT_i}{Dt} + n_i k T_i \frac{\partial u_\alpha}{\partial x_\alpha} &= - \frac{3}{2} k T_i R_i^{(0)} + \sum_j W_{ij}^{e(0)} + \sum_{jkl} W_{ij}^{hl(0)}, \end{aligned} \quad (1.3)$$

where  $u$  is the mean-mass velocity and  $T_i$  is the temperature of component  $i$  (molecules identical in structure but in different internal states are considered as belonging to different species),

$$\begin{aligned} \rho &= \sum_i m_i n_i, \quad p = k \sum_i n_i T_i, \\ \frac{D}{Dt} &= \frac{\partial}{\partial t} + u_\beta \frac{\partial}{\partial x_\beta}, \quad R_i^{(0)} \equiv \sum_{jkl} \int \frac{1}{2} I_{ij}^{kl}(f_0, f_0) dc_i = \sum_{jkl} [a_{kl}^{ij}(T_{kl}^*) n_k n_l - a_{kl}^{ij}(T_{ij}^*) n_i n_j], \\ T_{ij}^* &= \mu_j T_i + \mu_i T_j, \quad \mu_j = m_j m_{ij}^{-1}, \quad m_{ij} = m_i + m_j, \\ a_{ij}^{kl}(T) &= \frac{4}{\sqrt{\pi}} \left( \frac{\mu_{ij}}{2kT} \right)^{3/2} \langle g_{ij}^2 \rangle_{ij}^{kl} = \frac{q_k q_l}{q_i q_j} \left( \frac{\mu_{kl}}{\mu_{ij}} \right)^{3/2} \exp \left( \frac{E_{ij}^{kl}}{kT} \right) a_{kl}^{ij}(T), \\ \langle g_{ij}^2 \rangle_{ij}^{kl} &\equiv \int \exp \left( - \frac{\mu_{ij}}{2kT} g_{ij}^2 \right) g_{ij}^2 \sigma_{ij}^{kl} dg_{ij}, \quad \mu_{ij} = \frac{m_i m_j}{m_{ij}} \end{aligned}$$

$$\sum_i R_i^{(0)} \equiv 0, \quad \sum_i X_i^{(p)} R_i^{(0)} \equiv 0,$$

$$W_{ij}^{e(0)} \equiv \int \frac{m_i c_i^2}{2} \frac{1}{2} I_{ij}^e(f_0, f_0) dc_i = -16 \frac{n_i n_j \mu_{ij}}{m_{ij}} k(T_i - T_j) \Omega_{ij}^{(1,1)}(T_{ij}^*),$$

$$\Omega_{ij}^{(\alpha, \beta)} = \left( \frac{kT}{2\pi\mu_{ij}} \right)^{1/2} \int \exp(-g^2) g^{2\beta+3} Q_{ij}^{(\alpha)} dg,$$

$$Q_{ij}^{(\alpha)} = 2\pi \int (1 - \cos\alpha\chi) b db, \quad \sum_{ij} W_{ij}^{e(0)} = 0,$$

$$W_{ij}^{hl(0)} \equiv \int \frac{m_i c_i^2}{2} \frac{1}{2} I_{ij}^{hl}(f_0, f_0) dc_i = \left[ a_{hl}^{ij}(T_{hl}^*) \frac{3}{2} \mu_i \frac{kT_k T_l}{T_{hl}^*} n_k n_l - \right. \\ \left. - a_{ij}^{hl}(T_{ij}^*) \frac{3}{2} \mu_i \frac{kT_i T_j}{T_{ij}^*} n_i n_j \right] + \left[ b_{hl}^{ij}(T_{hl}^*) kT_{hl}^* \left( \mu_i \frac{T_k^2}{T_{hl}^{*2}} + \mu_k \frac{T_l^2}{T_{hl}^{*2}} - \mu_i \right) n_k n_l - \right. \\ \left. - b_{ij}^{hl}(T_{ij}^*) \mu_j \frac{kT_j^2}{T_{ij}^*} n_i n_j \right] + \left[ a_{hl}^{ij}(T_{hl}^*) \mu_j E_{hl}^{ij} - b_{hl}^{ij}(T_{hl}^*) \mu_j \mu_k \mu_l \frac{k(T_k - T_l)^2}{T_{hl}^*} \right] n_k n_l,$$

$$b_{hl}^{ij}(T) = \frac{4}{\sqrt{\pi}} \left( \frac{\mu_{hl}}{2kT} \right)^{5/2} \langle g_{hl}^5 \rangle_{ij} = \frac{q_i q_j}{q_h q_l} \left( \frac{\mu_{ij}}{\mu_{hl}} \right)^{3/2} \exp\left(-\frac{E_{hl}^{ij}}{kT}\right) b_{ij}^{hl}(T) - \frac{E_{hl}^{ij}}{kT} a_{hl}^{ij}(T), \quad \sum_{ijkl} W_{ij}^{hl(0)} = -\sum_i E_i R_i^{(0)};$$

where  $q_i$  is the degeneracy of the internal state of molecule  $i$ ;  $X_i^{(p)}$ , number of atoms (or combinations not destroyed in the reactions) of type  $p$  in molecule  $i$ ;  $\xi_i = c_i + u$ , molecular velocity;  $(1/2)I_{ij}^e$  and  $(1/2)I_{ij}^{kl}$ , integrals for the elastic and inelastic collisions,  $b$  is the central parameter; and  $f_{i0} = \frac{n_i}{n_i} \left( \frac{m_i}{2\pi kT_i} \right)^{3/2} \exp(-m_i c_i^2 / 2kT_i)$ .

The Navier-Stokes correction  $\varphi_{i1}$  needs to be known to obtain the equations in the Navier-Stokes approximation, and this satisfies the following linear integral equation:

$$f_{i0} \left[ \left( \frac{m_i c_i^2}{2kT_i} - \frac{5}{2} \right) c_i \nabla \ln T_i + \frac{p}{p_i} c_i d_{pi} + \frac{m_i}{kT_i} [c_i c_i] : \nabla u \right] + \\ + f_{i0} \left[ \frac{R_i^{(0)} + A_i}{n_i} - \frac{R_i^{(0)} + A_i}{n_i} \left( \frac{m_i c_i^2}{2kT_i} - \frac{3}{2} \right) + \frac{1}{p_i} \left( \frac{m_i c_i^2}{3kT_i} - 1 \right) (W_i^{e(0)} + W_i^{R(0)} + B_i) \right] - \\ - \sum_j \frac{1}{2} I_{ij}^e(f_0, f_0) - \sum_{jhl} \frac{1}{2} I_{ij}^{hl}(f_0, f_0) = I_{ii}^e(f_0, f_0 \varphi_{i1}) + \sum_j I_{ij}^{eS}(f_0, f_0 \varphi_{i1}) + \sum_{hij} I_{ij}^{hlS}(f_0, f_0 \varphi_{i1}). \quad (1.4)$$

The arbitrary constants  $A_i$  and  $B_i$  appearing in the inhomogeneous part of (1.4) have the properties  $\sum_i A_i = \sum_i X_i^{(p)} A_i = 0$ ,  $\sum_i B_i = -\sum_i E_i A_i$ , and with the arbitrary constants appearing in the

solution of the homogeneous equation allow one to construct  $\varphi_{i1}$  in such a way that the macroscopic parameters appearing in  $f_{i0}$  coincide with the true  $n_i$ ,  $u$ , and  $T_i$ .

In (1.4) we have used the symbols

$$p_i = n_i kT_i, \quad W_i^{e(0)} = \sum_j W_{ij}^{e(0)}, \quad W_i^{R(0)} = \sum_{jhl} W_{ij}^{hl(0)}, \quad d_{pi} = \nabla(p_i/p) \\ + (p_i/p - m_i n_i / \rho) \nabla \ln p, \quad [c_i c_i]_{\alpha\beta} = c_{i\alpha} c_{i\beta} - \delta_{\alpha\beta} c_i^2 / 3.$$

Analysis of the gasdynamic equations in the Navier-Stokes approximation falls outside the scope of this study. The contribution from  $\varphi_{i1}$  to  $R_i$ ,  $W_{ij}$  and  $W_{ij}^{kl}$  is determined as in the case of [16], and therefore we restrict ourselves to presenting the results from solving Boltzmann's equation by the generalized Chapman-Enskog method and consider the properties of the solution to (1.3).

2. The rate constants for the reactions appearing in the equations (or those for other inelastic processes occurring on collision)  $a_{ij}^{kl}$  are dependent on the combination of the translational temperatures  $T_{ij}^* = \mu_j T_i + \mu_i T_j$  [19]. The combination is such that  $T_{ij}^*$  is close to the temperature of the lighter molecules if the masses of molecules  $i$  and  $j$  differ considerably. This is an entirely natural result, because then the velocity of the lighter molecule makes the main contribution to  $g_{ij}$ , which controls  $\sigma_{ij}^{kl}$ . Further, the definition of  $a_{ij}^{kl}(T_{ij}^*)$  shows that the dependence of  $a_{ij}^{kl}$  on  $T_{ij}^*$  is functionally the same as the dependence of  $a_{ij}^{kl}$  on the gas temperature  $T$  when there is equilibrium in the translational temperatures, where  $T_i = T$ . This enables one to use standard theoretical and experimental data on  $a_{ij}^{kl}$  in calculations from (1.3). In relation to the latter we must note however that any corresponding experiment must satisfy the conditions for equilibrium in  $T_i: \tau_* \gg \tau_{\Delta}$ .

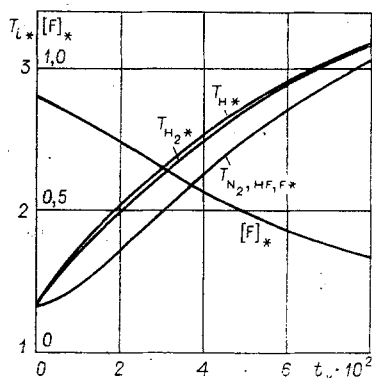


Fig. 1

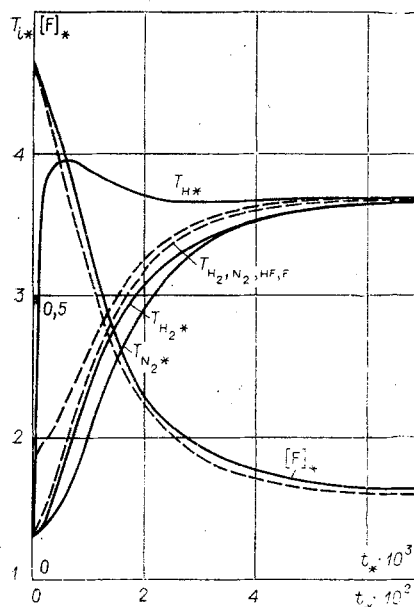


Fig. 2

The equations contain the new kinetic coefficients  $b_{ij}^{kl}$ , which differs from  $a_{ij}^{kl}$  in determining the rate of energy exchange between the components involved in the inelastic processes and chemical reactions. In certain cases one can state approximate relationships between the  $a_{ij}^{kl}$  and  $b_{ij}^{kl}$ ; e.g., the reaction may have a high energy threshold  $E_* \gg kT$ , whereupon it can be shown that if the cross section is only weakly dependent on the energy of the relative motion  $E_{ij}$  for  $E_{ij} > E_*$  (e.g., if the relationship is weaker than exponential), then for  $b_{ij}^{kl}$  we have the bound  $b_{ij}^{kl}(T) \approx (E_*/kT)a_{ij}^{kl}(T)$ . The model for the cross section

$$\sigma_{ij}^{kl} = \sigma_R [1 - E_*/E_{ij}] \chi(1 - E_*/E_{ij}) \quad (2.1)$$

is known as the model for reacting hard spheres [19], and then the relationship between  $b_{ij}^{kl}$  and  $a_{ij}^{kl}$  is established exactly:

$$b_{ij}^{kl}(T) = \left(2 + \frac{E_*}{kT}\right) a_{ij}^{kl}(T), \quad a_{ij}^{kl}(T) = \sigma_R \left(\frac{8kT}{\pi\mu_{ij}}\right)^{1/2} \exp\left(-\frac{E_*}{kT}\right).$$

In (2.1),  $\chi(z)$  is a Heaviside function. This model is used in the calculations here.

The terms  $W_{ij}^{(0)}$  in the equations for  $T_i$  are also dependent on the molecular interaction cross sections, which appear in the definition of the integrals  $\Omega_{ij}^{(1,1)}$ ; the latter can be expressed via the binary-diffusion coefficients  $[D_{ij}]_1$ , which are calculated to a first approximation from Sonin polynomials [20]:

$$\Omega_{ij}^{(1,1)} = \frac{3kT}{16n_{ij}\mu_{ij}[D_{ij}]_1}, \quad n_{ij} = n_i + n_j.$$

For the hard-sphere model used in the calculations,

$$\Omega_{ij}^{(1,1)}(T) = \sqrt{\frac{kT}{2\pi\mu_{ij}}} \sigma_{ij}, \quad \sigma_{ij} = \pi \left(\frac{d_i + d_j}{2}\right)^2,$$

where  $d_i$  is the diameter of the type  $i$  molecule.

3. We consider spatially homogeneous processes in a five-component mixture (two reactants  $A_i$  and  $A_j$ , the reaction products  $A_k$  and  $A_l$ , and the diluant  $A_N$ ). Here there are two characteristic situations. In one of these (formulation I), before the start of the reaction ( $t \leq 0$ ) the mixture will contain all five components, whose concentrations differ from the equilibrium ones for the initial temperature  $T_0$ . In the second, the mixture for  $t \leq 0$  consists only of  $A_i$ ,  $A_j$ , and  $A_N$  (formulation II). Let the molecules of all components have no rotational and vibrational degrees of freedom. We assume also that in all cases  $Y_i = n_i/n \sim Y_j \sim Y_R$ ,  $Y_k \sim Y_l$ ,  $Y_N \sim 1$  and that  $m_i \sim m_k \sim m$ ,  $m_j \sim m_l \sim M \gg m$ ;  $A_N$  is either a light ( $m_N \sim m$ ) or heavy ( $m_N \sim M$ ) component.

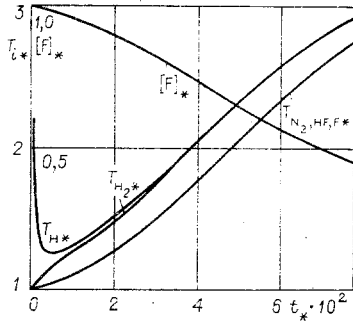


Fig. 3

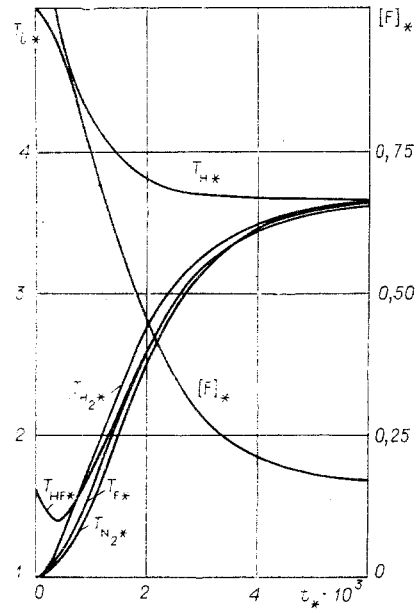


Fig. 4

For any  $m_N$ , the above  $\tau_\Delta$  is estimated by  $[n_*(2kT_{m^*}/m)^{1/2}\sigma_0(m/M)]^{-1}$ , where  $\sigma_0$  is the elastic-collision cross section, while  $n_*$  and  $T_{m^*}$  are the characteristic values of the total numerical density and the temperature for the light molecules. As  $\tau_R \sim [n_*Y_R(2kT_{m^*}/m)^{1/2}\sigma_R]$ , the multitemperature condition  $\tau_R \leq \tau_\Delta$  takes the form

$$(m/M) \leq Y_R(\sigma_R/\sigma_0). \quad (3.1)$$

The reaction causes the parameters (concentration and temperature for each of the components) to change in times  $\sim \tau_R$ , and therefore the description from the equations of gas-dynamics is applicable if  $\tau_R \gg \tau_0$ , where  $\tau_0$  is the time of Maxwellization of all the distributions. If  $m_N \sim M$ , this condition is obeyed for

$$\sigma_R/\sigma_{ij} = w \ll \min\left\{\left(\frac{1}{Y_R}\right)(T_{M^*}/T_{m^*})^{1/2}(m/M)^{1/2}, 1\right\}. \quad (3.2)$$

If  $m_N \sim m$ , we have instead of (3.2) that

$$w \ll (T_{M^*}/T_{m^*})^{1/2}(m/M)^{1/2}. \quad (3.3)$$

Obedience to (3.2) or (3.3) guarantees correct solution for formulation I in the system (1.3). However, the position alters for formulation II.

In fact,  $T_k$  and  $T_l$  for  $t = 0$  are naturally defined as

$$T_{k,l0} = \frac{2}{3k} \frac{W_{k,l}^{(0)}}{R_{k,l}^{(0)}} \Big|_{t=0} = T_0 \left[ 1 + \mu_{l,k} \left( \frac{1}{3} + \frac{2}{3} \frac{E_* + E_{ij}^{kl}}{kT_0} \right) \right]. \quad (3.4)$$

Here

$$3 \frac{\partial T_k}{\partial t} \Big|_0 = -16 \frac{m_l}{m_0} T_0 \left( \frac{1}{3} + \frac{2}{3} \frac{E_* + E_{ij}^{kl}}{kT_0} \right) \sum_{\alpha} n_{\alpha} \frac{m_k m_{\alpha}}{m_{k\alpha}^2} \Omega_{k\alpha}^{(1,1)}(T_{k\alpha}^*). \quad (3.5)$$

The expression for  $(\partial T_l/\partial t)_{t=0}$  is derived from (3.5) by permuting the subscripts  $k$  and  $l$ .

It follows from (3.5) that the temperature of the light product  $A_k$  for  $t \rightarrow 0$  changes in times of the order of  $f_k$ , the Maxwellization time, i.e., when the macroscopic description is inapplicable.

Therefore, formulation II is related to the problem of the initial conditions for (1.3), which is considered in the second part. Here we merely elucidate the sensitivity of the solution to the form of these conditions. As a result we get effective initial conditions, which are sufficient to obtain a solution with acceptable accuracy.

As an illustration we consider the reaction  $H_2 + F \rightleftharpoons HF + H$  in the presence of  $N_2$ . We take the following initial values for the parameters:  $Q/k = 4.8 \cdot 10^3$  K (30% of the 31.7 kcal/mole released in the reaction),  $E_*/k = 805^\circ$  K,  $d_{H_2} = d_H = 2.5$  Å,  $d_F = d_{HF} = d_{N_2} = 3.5$  Å,  $w =$

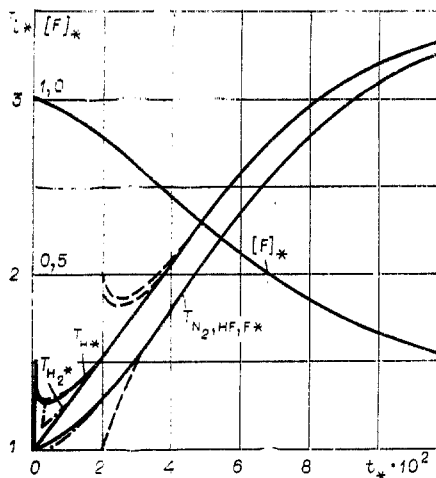


Fig. 5

0.55, molecular masses  $\mu(\text{H}) = 1$ ,  $\mu(\text{H}_2) = 2$ ,  $\mu(\text{F}) = 19$ ,  $\mu(\text{HF}) = 20$ ,  $\mu(\text{N}_2) = 28$ . Note that a reaction with this value of  $w$  does not satisfy (3.2) and (3.3), which is a feature usually neglected in calculations on pulsed HF lasers. To examine the solution to this problem for more correct conditions, we introduce two hypothetical mixtures having the parameters  $w_1 = 0.055$  for the initial masses of the molecules and  $w_2 = 0.011$  for  $\mu(\text{H}_2) = 0.02$ ,  $\mu(\text{F}) = 20.98$ ,  $\mu(\text{HF}) = 20.99$ ,  $\mu(\text{N}_2) = 28$  (the components are here denoted nominally).

In order to compare the results obtained for different initial compositions, we select the initial conditions for the temperatures of the components and the concentrations such that the final equilibrium state corresponds to a reaction beginning at  $T_{00} = 300^\circ\text{K}$  in a mixture:

$$[\text{H}_2]_{00} : [\text{F}]_{00} : [\text{N}_2]_{00} :: 0.3 : 0.3 : 0.4, \quad (3.6)$$

where the brackets denote the molar concentrations of the components. Therefore, in going to formulation I, where  $[\text{H}]_0 = [\text{HF}]_0 \neq 0$ , the initial temperature  $T_0$  is specified as  $T_0 = T_{00} + QY_{\text{H}_0}/k$ .

Figures 1-5 show the results. Figures 1 and 2 relate to formulation I. Figures 1-5 have the dimensionless time  $t_* = t/\tau_0$  as abscissa, where  $\tau_0$  is defined by  $p_0\tau_0 = 1 \text{ atm}\cdot\mu\text{sec}$  and  $p_0$  is the initial pressure of the mixture. The ordinate is the dimensionless temperature  $T_{1*} = T_1/T_{00}$  or the concentration  $[\text{F}]_* = [\text{F}]/[\text{F}]_{00}$ .

The data of Figs. 1-5 correspond to the following theoretical cases: Fig. 1 to the second hypothetical mixture,  $w = w_2$ :

$$[\text{F}]_0 : [\text{H}_2]_0 : [\text{HF}]_0 : [\text{H}]_0 : [\text{N}_2]_0 :: 0.27 : 0.27 : 0.03 : 0.03 : 0.40; \quad (3.7)$$

while Fig. 2 corresponds to the initial mixture (solid lines) and the first hypothetical mixture with  $w = w_1$  (broken curves), with the initial composition coinciding with (3.7); in the first case the large difference between  $T_{\text{H}}$  and  $T_{\text{H}_2}$  indicates that the macroscopic description is possible, but there is no marked difference in the  $T_1$ ; Fig. 3 corresponds to the second hypothetical mixture,  $w = w_2$ , with the composition at  $t = 0$  corresponding to (3.6), and conditions (3.1) and (3.2) are obeyed, but the feature connected with the initial layer is not eliminated; Fig. 4 is the initial mixture with the initial composition of (3.6), where the condition for a macroscopic description is not obeyed; and Fig. 5 is the second hypothetical mixture with  $w = w_2$ , where we show results for various initial conditions, which represent an analysis of the sensitivity to these conditions.

In the last case we vary the initial composition of the mixture (the calculations were performed for  $[\text{F}]_0/[\text{F}]_{00} = 0.999; 0.99; 0.90$ ) and also the distribution of the released energy between  $\text{H}_2$  and  $\text{H}$ . We found that the latter feature influences the solution only for a very short time interval after the start of the reaction. Effects of burnup of  $\text{F}$  amount in the main to shift of the curves on the  $t_*$  axis.

Figures 3 and 5 show that the effective initial conditions in formulation II can be either (3.4) and  $[\text{H}]_0 = [\text{HF}]_0 = 0$  or the conditions for formulation I when the burnup of  $\text{F}$  relative to the initial composition is reasonably small. In both cases we obtain virtually

identical results for the time dependence of the concentrations. An error occurs in the temperatures only for a very short time after  $t = 0$ .

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