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DYNAMICS OF A SINGLE BUBBLE IN A LIQUID IN THE PRESENCE OF CHEMICAL REACTIONS AND INTERPHASE HEAT AND MASS EXCHANGE

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The influence of inert and chemically reactive additives in the form of microdrops on the dynamics of a single bubble filled with an active gas mixture and collapsing under the action of a shock wave is considered. The development of a reaction during formation of the mixture is analyzed for instantaneous and dynamic evaporation of drops with allowance for various phases of their injection t_{inj}. *It is shown that in instantaneous evaporation, an increase in the fraction of gaseous argon in the* H_2+O_2 *system raises the final temperature of the system under cryogenic conditions, lowers it under ordinary conditions, and causes appreciable oscillations of the values of* γ, *heat release, and molecular weight. It is noted that there are values of* t_{inj} *and* D_0 *at which the final temperature of the mixture decreases practically to the initial temperature.*

As is known [1, 2], detonation of bubble media can be related to heat- and mass-transfer processes, whose rate increase markedly with development of instability of the bubble surface, which leads to formation of microdrops in them [3]. Evaporation of microdrops has a significant effect on the gas-phase chemical reaction in the bubble. Moreover, in a system where the fuel and oxidizer are in different phases [1], formation of a detonation wave is impossible without interphase heat and mass exchange, which leads to formation of a chemically reactive mixture. The detonation regime of the reactions in bubbles was studied in [4].

In the present work, as the first stage in the development of an adequate model for bubble detonation in such media, we consider the influence of inert and chemically reactive additives in the active gas mixture of a bubble on bubble dynamics and explosive process, and reaction propagation during formation of the mixture. The dependences of the parameters of a single bubble on the time of injection t_{inj}, the initial dimensions of microdrops D_0, and the mass of evaporated liquid M_L are analyzed in the case of instantaneous evaporation of microdrops and with allowance for evaporation dynamics.

Bubble dynamics is described by the Rayleigh equation under the assumption that the bubble retains its spherical shape, and the gas is ideal:

$$\beta\beta'' + \frac{3}{2}\beta' = P - P_\infty.$$

Here $\beta = R/R_0$ is the dimensionless radius of the bubble, β' and β'' are the derivatives of β with respect to the dimensionless time $\tau = (\sqrt{P_0/\rho_L}/R_0)t$ (ρ_L is the liquid density and t is time), R and R_0 are the current and initial radii of the bubble, P_∞ is the external pressure referred to the initial pressure P_0, and P is given by the following relation, which takes into account losses in acoustic radiation of the bubble:

$$P = \frac{1}{P_0}\Big(\rho_g \frac{\mathfrak{R}T}{\mu} - \frac{2\sigma}{R}\Big) - \frac{4\beta'}{\beta\mathrm{Re}} + \frac{1}{c_0}\sqrt{\frac{P_0}{\rho_L}}\Big(1 + \frac{P_g - P_\infty}{B_1 - P_\infty}\Big)^{-1/n}\beta\,\frac{dP_g}{d\tau};$$

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ρ_g is the gas density, $B_1 = B/P_0$ and n are the constants of the Tait equation, c_0 is the velocity of sound in the liquid, $\mathfrak{R}$ is the universal gas constant, $\mathrm{Re} = (R_0/\nu_L)\sqrt{P_0\rho_L}$ is the Reynolds number, ν_L is the dynamic viscosity of the liquid, μ is the molar weight of the gas, σ is the surface-tension coefficient of the liquid, and $P_g = (\rho_g/P_0)(\mathfrak{R}T/\mu)$ is the pressure of the gas.

It is assumed that before a lapse of the induction time, the state of the gas-vapor mixture corresponds to a chemically nonreactive gas, and after induction, it corresponds to a gas in chemical equilibrium. The induction period t_{sr} is defined by the conventional condition

$$\int_0^{t_{sr}} \frac{dt}{\tau_i} = 1,$$

where $\tau_i = (A_i/\eta)\exp(E_a/(\mathfrak{R}T))$ is the induction period at constant parameters [5] [$\eta = (\rho/\mu)(\nu_{\mathrm{H}_2}\nu_{\mathrm{O}_2})^{-1/2}$, ν_{H_2} and ν_{O_2} are the molar fractions of H_2 and O_2 respectively], and A_i and E_a are constants.

The thermodynamic parameters of the mixture are calculated by the approximate model of kinetics of [6], which has high accuracy, and without using the adiabat of an inert gas, which is commonly used in such problems. The model of kinetics includes the isentropic equation

$$\frac{dT}{d\tau} = \frac{dT}{d\rho}\frac{d\rho}{d\tau} = \Big(-\frac{U_\mu \mu_\rho - \mathfrak{R}T/(\rho\mu)}{U_T + U_\mu \mu_T}\Big)\Big(-3\rho_0\frac{\beta'}{\beta^4}\Big)$$

and the equation of chemical equilibrium [6]

$$\frac{\rho_g}{\mu}\frac{(1-\mu/\mu_{\max})^2}{\mu/\mu_{\min}-1}\exp(E_D/(\mathfrak{R}T)) = \frac{AT^{3/4}}{4K_+}(1-\exp(-\theta/T))^{3/2}. \qquad (1)$$

Here T and U are the temperature and internal energy of the gas, $dT/d\rho = -(U_\mu \mu_\rho - \mathfrak{R}T/(\rho\mu))/(U_T + U_\mu \mu_T)$ [7], $d\rho/d\tau = -3\rho_0(\beta'/\beta^4)$, U_μ, U_T, μ_T, and μ_ρ are the derivatives with respect to the parameters denoted by the subscripts, ρ_0 is the initial density of the gas, $\mu_{\min}$ and $\mu_{\max}$ are the molar weights in the completely dissociated and completely recombined state, and E_D is the average energy of dissociation of the reaction products. In this case, the internal energy of the gas is given by the formula [6, 8]

$$U = \Big[\frac{3}{4}\Big(\frac{\mu}{\mu_a}+1\Big) + \frac{3}{2}\Big(\frac{\mu}{\mu_a}-1\Big)\frac{\theta/T}{\exp(\theta/T)-1}\Big]\frac{\mathfrak{R}T}{\mu} + E_D\Big(\frac{1}{\mu}-\frac{1}{\mu_{\min}}\Big),$$

where μ_a is the molar weight in the atomic state, θ is the effective temperature of excitation of the vibrational degrees of freedom of the molecules, A and K_+ are the rate constants for the dissociation and recombination of the generalized products of the reaction. The quantities μ_a, $\mu_{\min}$, and $\mu_{\max}$ are determined by the composition of the gas and, hence, they remain constant up to the moment $t = t_{\mathrm{inj}}$, when they undergo a jump, and then they do not vary. The magnitude of the jump depends on the chemical composition and mass of the evaporated liquid [8].

The indicated model is applicable for oxygen–hydrogen systems of any chemical composition (including systems with inert components). It allows one for the first time to take into account the strong changes in the molecular weight, isentropic exponent, heat capacities, and the heat effect of the chemical reactions due to the recombination and dissociation processes and the variation in the fuel–oxidizer ratio in the gas phase. For example, for mixture I [H_2 (gas)–O_2 (liquid) under cryogenic initial conditions], the molecular weight of the gas can change by an order magnitude.

After a lapse of the induction time ($t = t_{sr}$), the gas instantaneously enters the state of chemical equilibrium, which is continuously shifted owing to bubble dynamics. The instantaneous change in the gas parameters at the jump was calculated from the equation of chemical equilibrium (1) and the condition $U_1 = U_2$, where U_1 and U_2 are the internal energies of the gas before and after the jump. The radius of the bubble, the gas density, and the parameters μ_a, $\mu_{\min}$, and $\mu_{\max}$ at the moment of jump do not change.

Instantaneous Evaporation. The gas bubble oscillates in the liquid in the field of instantaneously applied constant external pressure. The real processes of heat and mass exchange are replaced by instantaneous single evaporation of the liquid of mass M_L at time t_{inj} from the beginning of compression. At the moment

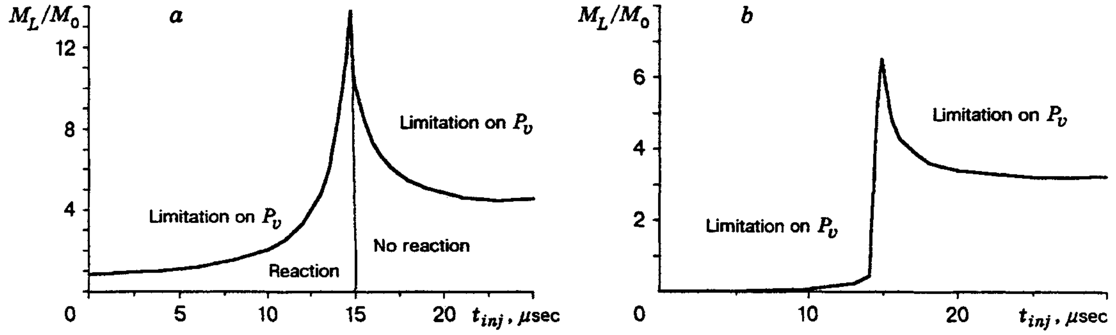

Fig. 1

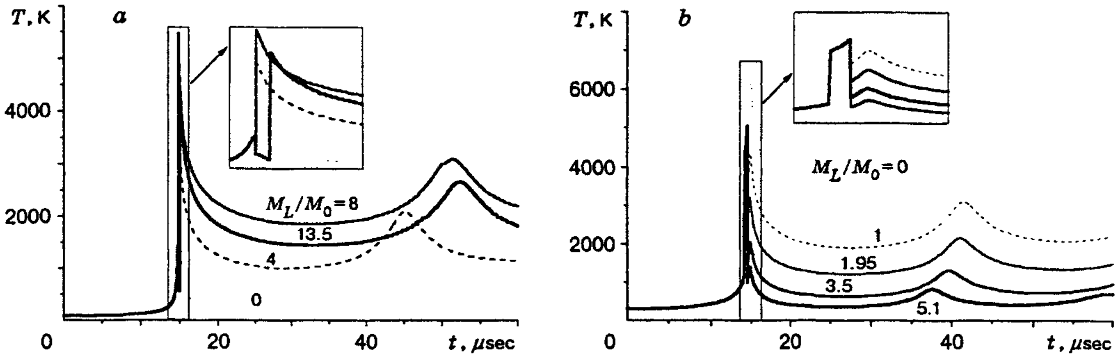

Fig. 2

the liquid of mass M_L is evaporated, the thermodynamic parameters and composition of the gas change by a jump, whose magnitude at constant time and radius of the bubble is calculated in three stages.

1. The mass M_2 of the bubble gas and its density after evaporation of the liquid are calculated on the basis of the law of conservation of mass $M_0 + M_L = M_2$, where M_0 is the initial mass of the gas in the bubble.

2. The parameters μ_a, $\mu_{\min}$, and $\mu_{\max}$ after evaporation are calculated from the value of M_2 and the known initial compositions of the gas and the liquid using the algorithm of [8].

3. The pressure and temperature of the gas after evaporation are determined from the equation of state and the energy conservation law $U_1 + U_L = U_2$, where U_1 and U_2 are the internal energies of the gas before and after the moment of evaporation and U_L is the internal energy of the liquid. If evaporation occurs before the end of the induction period, the molecular weight of the gas μ is calculated according to [8]; otherwise, μ is calculated from (1).

The above model was used to calculate bubble dynamics with variation in τ_{inj} and M_L for mixtures I and II [$2H_2 + O_2$ (gas)–H_2O (liquid)] with and without an inert diluent. The calculations were performed for the following initial parameters: $T_0 = 87$ K (in mixture I), $T_0 = 293$ K (in mixture II), initial pressure of the bubble gas $P_0 = 1.011 \cdot 10^5$ Pa, external pressure $P_\infty = 100\,P_0$, and $R_0 = 1.6$ mm. The remaining constants were taken from [7, 9].

In the calculations, we verified satisfaction of the condition on the partial pressure of the evaporated component, which cannot exceed the pressure of the corresponding saturated vapor P_v. The result in the form of a region where the solutions have a physical sense is shown in Fig. 1a for mixture I and Fig. 1b for mixture II.

The calculations showed that the dependences of the gas parameters on M_L are different for mixtures I (Fig. 2a) and II (Fig. 2b). For example, in mixture I ($t_{\text{inj}} = 14.7$ μsec), the average temperature of the bubble

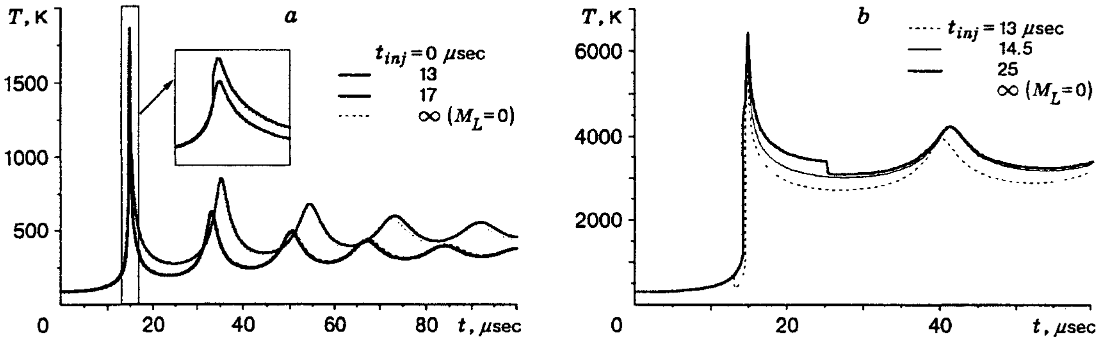

Fig. 3

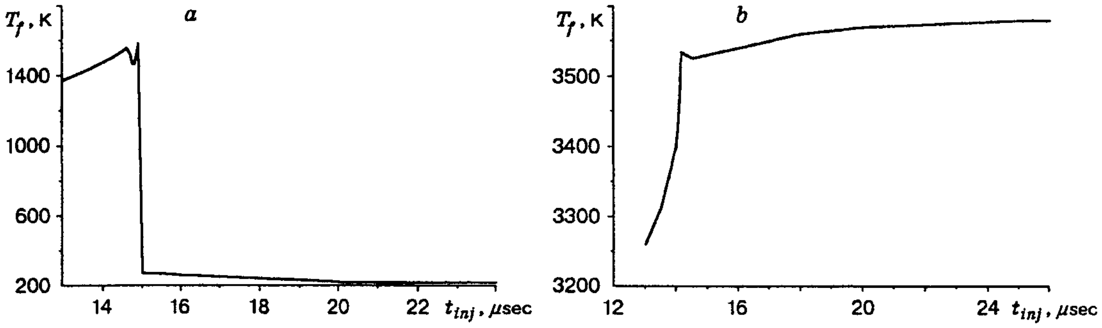

Fig. 4

gas passes through a maxima with increase in M_L, and in mixture II ($t_{\rm inj} = 14.5$ μsec), an increase in M_L leads to a monotonic decrease in the temperature of the bubble gas.

As shown in [10], use of only the "pure" kinetics of chemical reactions to describe bubble detonation does not lead to formation of a solitary wave. The temperature distribution after attainment of a steady-state regime of the process with the amplitude and velocity corresponding to experiment indicates that the detonation wave has an unduly long "tail," whose amplitude is close to the amplitude of the initiating wave. Obviously, the mechanism of formation of a solitary wave can be determined by intense evaporation of the liquid, which decreases the gas temperature and pressure in the "tail" of the bubble-detonation wave. Thus, from Fig. 2b it follows that evaporation of a small amount of liquid (comparable in order of magnitude with the mass of the gas bubble) reduces the final temperature of the gas practically to the initial temperature.

Figure 3 shows the variation in the gas temperature for various $t_{\rm inj}$ (Fig. 3a refers to mixture I with $M_L/M_0 = 0.4$ and Fig. 3b refers to mixture II with $M_L/M_0 = 5.1$). According to the calculations, the variation in the gas parameters and the parameter values after oscillation damping can significantly depend on $t_{\rm inj}$ if the latter is close to the moment of maximum compression of the bubble. Otherwise, the gas parameters depend on injection time weakly, as shown in Fig. 4 (Fig. 4a refers to mixture I with $M_L/M_0 = 4$ and Fig. 4b refers to mixture II with $M_L/M_0 = 0.23$). We note that the low value of T_f in mixture I at $t_{\rm inj} \geqslant 15$ μsec is due to the fact that the decrease in the gas temperature in the bubble caused by evaporation increases the induction period considerably, which in combination with acoustic losses of the bubble leads to "failure" of the reaction.

The influence of an inert diluent (argon) on the gas temperature in mixture I is shown in Fig. 5. Curve 1 illustrates the process with evaporation of liquid oxygen at $M_{L({\rm I})} = 0.43\,M_0$ with no argon in the gas. Addition of an equal molar fraction of argon to the gas phase at the same ratio of M_L/M_0 increases the gas temperature sharply (curve 2). We note that in this case, the mass of the evaporated liquid M_L is larger since M_0 increases with addition of argon, and the proportion of hydrogen and evaporated oxygen approaches

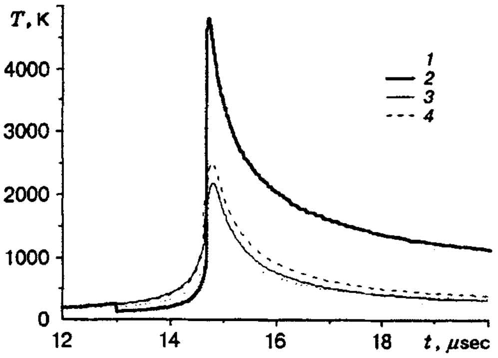

Fig. 5

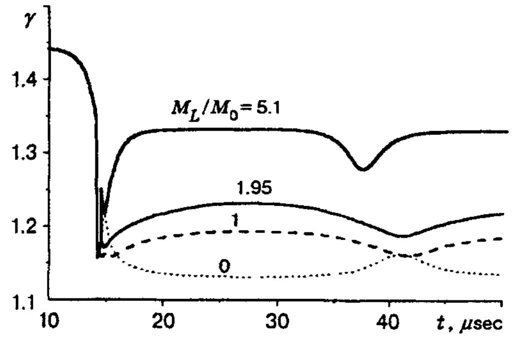

Fig. 6

stoichiometry, which enhances energy release. Nevertheless, when the proportion of hydrogen and oxygen is the same as in the first case, the presence of argon increases the gas temperature (curve 3). If $M_L = M_{L(\mathrm{I})}$ is evaporated, the gas temperature also increases (curve 4). In addition, the calculations show that an increase in the fraction of gaseous argon in a bubble always raises the final temperature in mixture I and lowers it in mixture II. In both cases, the pressure and degree of compression decrease and the temperature in the first oscillation increases.

Figure 6 presents the curve of the isentropic exponent γ versus M_L for mixture II at $t_{\mathrm{inj}} = 14.5$ μsec, from which it follows that evaporation leads to considerable fluctuations of the value of γ. Allowance for this factor is of fundamental importance and is a merit of the approach proposed here.

Continuous Evaporation. Under real conditions, microdrops do not evaporate instantaneously. In this connection, as the following steps in the modeling of the gas-phase processes, it is assumed that at time t_{inj}, a system of liquid microdrops with diameter D_0 and total mass M_L originates instantaneously in the bubble. In each integration step, continuous evaporation of the microdrops is modeled by instantaneous evaporation of mass Δm, which is determined from the current diameter of a microdrop D using the known equation of combustion of a liquid drop in a gas [11]:

$$\frac{dD}{dt} = -k' \frac{\mathrm{Nu}}{4D},$$

where the evaporation constant k' is calculated from the formula

$$k' = \frac{8k_g}{\rho_L c_p} \ln\left(\frac{L + c_p \Delta T}{L}\right).$$

Here k_g is the thermal conductivity of the combustion products, c_p is the heat capacity at constant pressure, L is the heat of vaporization, ρ_L is the liquid density, $\mathrm{Nu} = hD/k_g$ is the Nusselt number, and h is the heat-transfer coefficient. If the current temperature of the bubble gas becomes lower than the initial temperature, it is assumed that the microdrops do not evaporate ($dD/dt = 0$).

The jump of the parameters and their subsequent variations were calculated by the same algorithm and under the same assumptions as in the case of instantaneous evaporation of microdrops.

Figure 7 shows the variation in the relative mass of microdrops m/m_0 with time at $t_{\mathrm{inj}} = 13$ μsec and $M_L/M_0 = 0.45$ for mixture II. Curves 1–3 correspond to initial diameters of 1, 5, and 15 μm, respectively. For comparison of the evaporation of a microdrop and bubble dynamics, the dashed curve shows the variation in the bubble radius β at $D_0 = 5$ μm. It is obvious that microdrops with a size of about 1 μm evaporate practically instantaneously (in a time much shorter than the oscillation period of a bubble). For microdrops with a size larger than 5 μm, it is important to take into account that the time of evaporation is finite.

As in the case of instantaneous evaporation of microdrops, we verify satisfaction of the condition on the pressure of the saturated vapor P_v. In this case, the total volume of microdrops at each time must be less than the bubble volume.

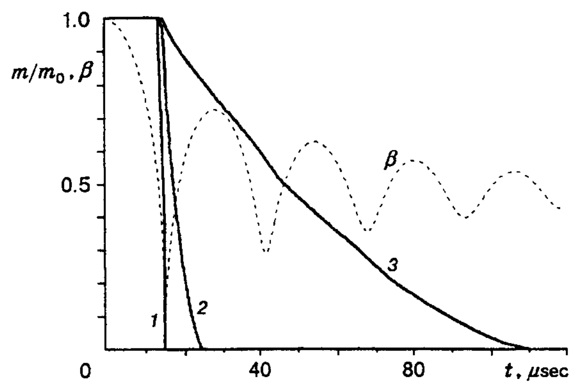

Fig. 7

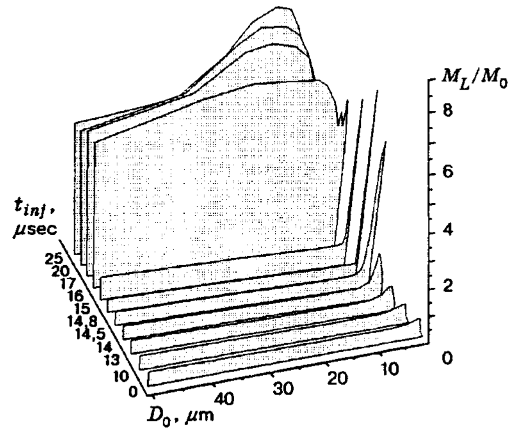

Fig. 8

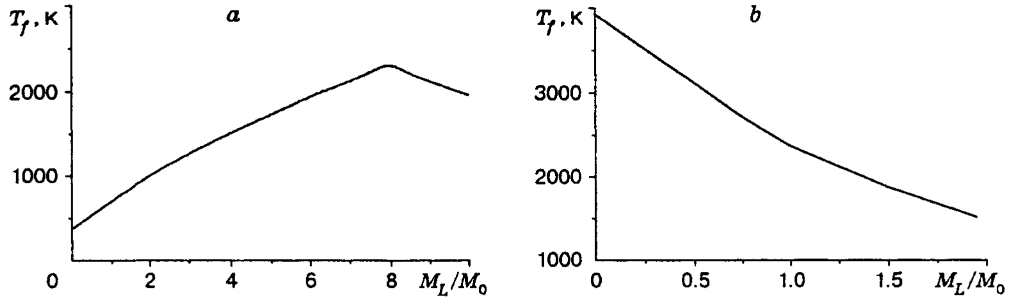

Fig. 9

For the case of continuous evaporation, the region of existence of solutions, dissected by planes (M_L, D_0), in which the specified conditions in mixture II are satisfied is shown in Fig. 8. For mixture I, a similar region of physical solutions with the fundamental difference that the maximum value $M_L/M_0 = 12$ is reached for $D_0 = 0$ and $t_{\text{inj}} = 14.5$ μsec is obtained. The section of such three-dimensional regions by the plane (M_L, t_{inj}) at $D_0 = 0$ is a two-dimensional region of physical solutions for the case of instantaneous evaporation of the liquid (see Fig. 1b). The sharp increase in the largest possible value of M_L/M_0 for the sections $t_{\text{inj}} \geqslant 16$ μsec is caused by the increase in the saturated vapor pressure due to the increase in the gas temperature as a result of the chemical reaction and adiabatic compression of the bubble. For any t_{inj}, the curve of M_L/M_0 versus D_0 has a maximum. The initial diameter of the microdrops D_0 that corresponds to the maximum is 1–1.5 μm for $t_{\text{inj}} < t_{sr}$, 0 for $t_{sr} < t_{\text{inj}} < t_{\max}$, and about 10 μm for $t_{\max} < t_{\text{inj}}$, where $t_{\max}$ is the moment of maximum compression of the bubble.

Let us illustrate the effect of the amount of the injected liquid on the process considered and the gas parameters in the bubble. Figure 9 shows a curve of the final (after damping of bubble oscillations) gas temperature T_f versus the value of M_L/M_0 for mixture I at $t_{\text{inj}} = 14$ μsec and $D_0 = 0.75$ μm (Fig. 9a) and mixture II at $t_{\text{inj}} = 14$ μsec and $D_0 = 1$ μm (Fig. 9b). It is obvious that an increase in the mass of the injected liquid in mixture II leads to a monotonic decrease in the final temperature. As calculations show, the ratio of T_f to the maximum temperature attained in the first oscillation also decreases from ~0.6 to ~0.3. A decrease in T_f leads to a slight monotonic increase in the final values of μ and γ, and μ reaches a maximum value $\mu_{\max}$ already at $M_L/M_0 = 1$, after which it remains constant. In the case considered, $T_f > T_0$. However, there are values of the parameters t_{inj} and D_0 (for example, $t_{\text{inj}} \sim 15$ μsec and $D_0 \sim 1$ μm) at which the final gas temperature decreases practically to the initial value.

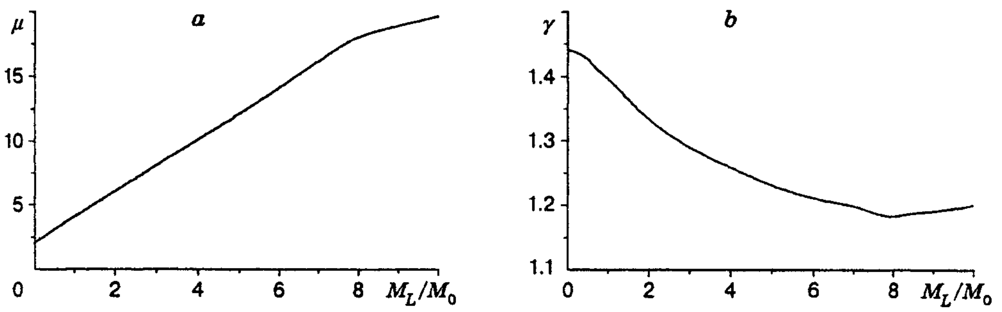

Fig. 10

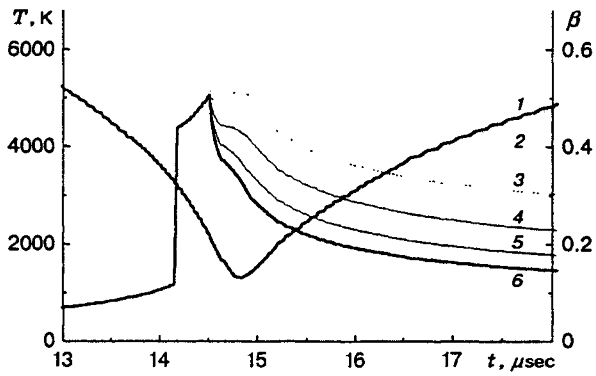

Fig. 11

For mixture I, the dependences of T_f, μ, and γ on M_L/M_0 are fundamentally different. With increase in M_L/M_0, the value of T_f passes through a maximum (Fig. 9a), which corresponds to the stoichiometric fuel–oxidizer ratio. In this case, γ passes through a minimum (Fig. 10b), and μ increases by an order of magnitude (Fig. 10a) ($t_{\text{inj}} = 14$ μsec and $D_0 = 1$ μm).

Figure 11 shows the variation in the gas temperature and bubble radius in the first oscillation in mixture II. The calculations are performed for various M_L/M_0 at $t_{\text{inj}} = 14.5$ μsec and $D_0 = 1$ μm. Curves 1–5 correspond to the temperatures at values of M_L/M_0 equal to 0, 0.5, 1, 1.5, and 1.95. Integer 6 designates the set of curves of β (which are poorly differentiable on the scale of Fig. 11) constructed for the specified values of M_L/M_0. The jump of temperature at $t = 14.2$ μsec is associated with the beginning of the chemical reaction. The decrease in the gas temperature T due to an increase in M_L/M_0 is predictable, but it is interesting that its maximum is reached at the moment of maximum collapse of the bubble only for values of M_L/M_0 smaller than 0.5. For the remaining M_L/M_0, the decrease in the temperature due to intense evaporation of a considerable amount of the liquid is more considerable than its growth due to the decrease in the bubble radius. For such M_L/M_0, the maximum temperature is reached at the initial moment of evaporation of microdrops t_{inj}. With increase in D_0, the rate of evaporation of the liquid decreases, and, therefore, the limiting value of M_L/M_0 at which the maximum temperature corresponds to the maximum collapse of the bubble grows. Irrespective of the value of M_L/M_0, the maximum temperature in mixture I corresponds to maximum compression.

The dependences of T_f on the diameter of microdrops for fixed values of M_L/M_0 and t_{inj} are qualitatively identical for mixtures I and II. The value of T_f grows monotonically with increase in D_0 and tends to constant values of 800 and 3200 K, respectively.

In the case of continuous evaporation of microdrops, introduction of the additional parameter D_0 can significantly change the parameters of the process considered. Thus, for mixture I, the dependence of T_f on t_{inj} qualitatively corresponds to Fig. 4a. For mixture II at $D_0 \leqslant 3$ μm, this dependence is similar to the one shown in Fig. 4b, and for large D_0, the value of T_f does not depend on t_{inj}.

REFERENCES

1. A. V. Pinaev and A. I. Sychev, "Detection and investigation of self-sustaining detonation regimes in systems of a liquid fuel and oxidizer bubbles," *Dokl. Akad. Nauk SSSR*, **290**, No. 3, 611–615 (1986).
2. A. V. Pinaev and A. I. Sychev, "Structure and properties of detonation in liquid–gas bubble systems," *Fiz. Goreniya Vzryva*, **22**, No. 3, 109–118 (1986).
3. A. V. Dubovik and V. K. Bobylev, *Sensitivity of Liquid Explosive Systems to Impact* [in Russian], Nauka, Moscow (1978).
4. A. A. Vasil'ev, V. K. Kedrinskii, and S. P. Taratuta, "Dynamics of a single bubble with a chemically active gas," *Fiz. Goreniya Vzryva*, **34**, No. 2, 121–124 (1998).
5. D. R. White, "Density induction times in very lean mixtures of D_2, H_2, C_2, $C_2 H_2$ and $C_2 H_4$ with O_2," in: *XI Int. Symp. on Combustion*, Academic Press, Pittsburgh (1967), pp. 147–154.
6. Yu. A. Nikolaev and D. V. Zak, Agreement of models of chemical reactions in gases with the second law of thermodynamics," *Fiz. Goreniya Vzryva*, **24**, No. 4, 87–90 (1988).
7. P. A. Fomin and A. V. Trotsyuk, "An approximate calculation of the isentrope of a gas in chemical equilibrium," *Fiz. Goreniya Vzryva*, **31**, No. 4, 59–62 (1995).
8. Yu. A. Nikolaev and P. A. Fomin, "Approximate equation of kinetics in heterogeneous systems of the gas-condensed-phase type," *Fiz. Goreniya Vzryva*, **19**, No. 6, 49–58 (1983).
9. I. S. Grigor'ev and E. Z. Meilikhova (eds.), *Physical Quantities: Handbook* [in Russian], Energoatomizdat (1991).
10. V. K. Kedrinskii, F. N. Zamaraev, and Ch. Meider, "Waves in a chemically active bubble medium," *Prikl. Mekh. Tekh. Fiz.*, No. 2, 20–26 (1990).
11. S. Lambiris and L. Combs, "Experimental study of stationary combustion of mixture of liquid oxygen with kerosine in rocket chamber and theory of combustion of pulverized jet," in: *Detonation and Two-Phase Flow*, Academic Press, New York–London (1962).