NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL MEMORANDUM 1296

ON THE THEORY OF COMBUSTION OF INITIALLY UNMIXED GASES

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INTRODUCTION

The chemical reaction of two substances (fuel and oxygen) accompanied by the formation of new substances of the products of combustion and the liberation of heat is considered.

A steady process with a continuous supply of the initial substances and a removal of the products is assumed. The particular feature of the case under consideration is that the fuel and the oxygen or air are individually supplied, that is, they are not initially mixed. It follows that even in the case where the constant of the reaction velocity of the oxygen with the fuel is large the intensity of combustion does not exceed a certain limit, which depends on the mixing rate of the fuel and the oxygen.

The combustion itself essentially changes the distribution of the concentrations as compared with the distribution of the concentrations in the mixing of the same gases without combustion.

It has long been established (as far back as Faraday if not earlier) as a fundamental qualitative characteristic of combustion that the surface of the flame separates a region in which there is oxygen and no fuel (the oxidizing region) from a region in which there is no oxygen but only fuel.

Burke and Schumann (reference 1) considered the shape of the flame surface in a very particular case of combustion in parallel concentrated laminar flows of the fuel and oxygen or air. They did not consider in detail the phenomena occurring in the flame region.

The most complete recent work is that of Shvab (reference 2), which appeared at Leningrad in 1940. In this work, a detailed study is made of a turbulent flame torch; the study considers both the case of the supply of a pure gas fuel and the case of the supply of a gas mixture with insufficient amount of air. Shvab found relations between the

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fields of concentration of the gas, the oxygen, and the product of combustion and the temperature and the velocity field of the gas. A number of the results obtained by Shvab (in particular, the constancy of the concentration of the products of combustion and of the temperature) on the surface of the flame are presented, for completeness, in the present article.

The discussion given of the reaction zone and the kinetics of the chemical reaction (section 5) is new.

For laminar combustion, it is possible on the basis of this investigation to proceed further and explain the limits of the possible intensity of combustion, depending on the fact that for a large rate of fuel and oxygen supply to the flame surface the velocity of the chemical reaction is not sufficient.

1. GENERAL EQUATIONS

A region is considered in which the gas moves with velocity $\vec{w}$, the density of the gas is ρ, the concentration by weight of the component of interest is a, the coefficient of diffusion is D, the heat conductivity is λ, the temperature conductivity is $\lambda/a\rho = \kappa$, and the temperature is T; all these magnitudes that depend on the coordinates are variable. The flow of component a is given by the equation

$$\vec{q}_a = \rho a \vec{w} - \rho D \operatorname{grad} a \tag{1}$$

The vector $\vec{q}_a$ gives the direction of the flow and its magnitude in grams per square centimeter in seconds at a given point. The general equation of diffusion has the form

$$\operatorname{div} \vec{q}_a = L(a) = -\frac{\partial}{\partial t}(\rho a) + F_a \tag{2}$$

The left side of equation (2) gives the divergence of the flow, that is, the difference between the amount carried away by the flow and the amount of substance supplied by the flow referred to unit volume, and the right side gives the change in the amount of substance a in unit volume $\partial(\rho a)/\partial t$ and the amount of substance a transformed in unit volume as a result of the chemical reaction.

The differential operator is denoted by the symbol L(a)

$$L(a) = \operatorname{div}\left(\rho a\vec{w}\right) - \operatorname{div}\left(\rho D \operatorname{grad} a\right) \tag{3}$$

In steady flow,

$$\left.\begin{aligned} \frac{\partial}{\partial t}(\rho a) &= 0 \\ \frac{\partial \rho}{\partial t} = -\operatorname{div}\left(\rho\vec{w}\right) &= 0 \end{aligned}\right\} \tag{4}$$

$$L(a) = \rho\vec{w} \operatorname{grad} a - \operatorname{div}\left(\rho D \operatorname{grad} a\right) \tag{5}$$

For a steady process,

$$L(a) = F_a \tag{6}$$

The equation of heat conductivity has the analogous form (neglecting the heat transferred by radiation)

$$\vec{q}_T = \rho T c\vec{w} - \lambda \operatorname{grad} T = \rho T c\vec{w} - \varkappa c\rho \operatorname{grad} T \tag{7}$$

where c is the specific heat, which is assumed constant. Then

$$\operatorname{div}\vec{q}_T = cL(T) = -c\frac{\partial}{\partial t}(\rho T) + Q \tag{8}$$

where Q is the volume rate of the heat transfer.

In a steady process,

$$L(T) = \frac{Q}{c} \tag{9}$$

If the coefficients of diffusion of the initial substances a and b and of the products of combustion g and h and the coefficient of heat conductivity are all equal to each other,

$$D_a = D_b = D_g = D_h = \kappa = D \tag{10}$$

the operators L(a), L(b),..., L(T) are all the same in the formulas of the type of equation (6) for the different substances and formula (9) for the temperatures.

In the chemical reaction of combustion, the quantities of the initial substances entering the reaction, the quantities of the transformed products of combustion, and the quantity of heat given out are in definite, strictly constant, relations to one another. With the volume rate of the reaction denoted by F, all the magnitudes can be expressed in terms of it

$$\left.\begin{aligned} F_a &= -\frac{F}{\alpha} \\ F_b &= -\frac{F}{\beta} \\ F_g &= \frac{F}{\gamma} \\ F_h &= \frac{F}{\eta} \\ \frac{Q}{c} &= \frac{F}{\tau} \end{aligned}\right\} \tag{11}$$

with the aid of the constant positive coefficients $\alpha,\ldots,\tau$. The signs in equations (11) correspond to the fact that a and b are expended and g, h, and the heat are given out in the reaction. The coefficients $\alpha,\ldots,\tau$ are put in the denominators for convenience in the further discussion. Example:

$a = CH_4$

$b = O_2$

$g = CO_2$

$$h = H_2O$$

$$\bar{c} = 0.5 \text{ cal/(gram)(}^\circ\text{C)}$$

heat of reaction 192,000 (cal/mole) CH_4.

By expressing F as the expenditure of all substances entering the reaction in grams per cubic centimeter per second, there are obtained the values

$$\alpha = 5$$

$$\beta = 1.25$$

$$\gamma = 1.82$$

$$\eta = 2.22$$

$$\tau = 1/4800^\circ = 2.08 \cdot 10^{-4}(^\circ C)^{-1}$$

With the aid of these coefficients, all the differential equations of diffusion of the different substances and the equations of heat conduction during the chemical reaction assume like form with equal L and F in all formulas

$$\left.\begin{aligned} L(\alpha a) &= -F \\ L(\beta b) &= -F \\ L(\gamma g) &= F \\ L(\eta h) &= F \\ L(\tau T) &= F \end{aligned}\right\} \qquad (12)$$

It is yet impossible to conclude the similarity of the fields of all the magnitudes a,..., T of interest, for the field of each magnitude depends not only on the differential equation that it satisfies but also on the boundary conditions.

The fuel gas is supplied through one pipe (I); correspondingly, within the pipe

I.

$$\left.\begin{array}{r} a = a_0 \\ b = g = h = 0 \\ T = T_0 \end{array}\right\} \qquad (13)$$

where a_0 is the concentration of the fuel in the gas to be burned. This gas may be diluted, for example, with nitrogen. Air is supplied through the other pipe (II)

II.

$$\left.\begin{array}{r} b = b_0 \\ a = g = h = 0 \\ T = T_0 \end{array}\right\} \qquad (14)$$

where b_0 is the concentration of the oxygen in the air. In the combustion of a torch in the free atmosphere, condition II refers not to the air pipe but to the concentrations in the atmosphere at an infinite distance from the torch.

At the surface of the pipe or a burner, the boundary conditions consist of the fact that the flow of any substance through the material surface is equal to zero, so that the component of the correspondent vector normal to the surface is equal to zero. These conditions are the same for all substances. The boundary conditions for the temperature will be the same as the boundary conditions for $a, \ldots, h$, if heat is not abstracted from the torch, that is, if only heat-insulating and not heat-emitting surfaces are considered or if, in general, the walls with the temperature T_0 are located only where the temperature of the gases is equal to T_0.

These conditions are assumed satisfied so that the boundary conditions for all substances and the temperatures at the walls are the same.

2. ANALYSIS OF EQUATIONS: EQUATION OF FLAME SURFACE

An analysis of the equations is now made. The principal difficulty in the direct solution of the equations lies in the fact that the velocity of the reaction F depends greatly on the required magnitudes a, b, and T.

By subtracting the first equation from the second equation there is obtained

$$\left.\begin{aligned} L(\alpha a - \beta b) = L(p) = 0 \\ \text{where} \qquad \\ p = \alpha a - \beta b \end{aligned}\right\} \qquad (15)$$

with the boundary conditions

$$\left.\begin{aligned} \text{I)}\ p = \alpha a_0 \\ \text{II)}\ p = -\beta b_0 \end{aligned}\right\} \qquad (16)$$

Thus the difference in concentrations of the fuel and the oxygen, taken with the corresponding stoichiometric coefficients, is subject to the equation of diffusion in which the velocity of reaction F does not enter. This equation was considered by Burke and Schumann for determining the shape of the flame on the assumption that the fuel can be considered as negative oxygen. If combustion rather than a slow reaction is considered, the function F for simultaneous $a \neq 0$, $b \neq 0$ is very large. Because the total quantity of substance burning in unit time is restricted by the amount of fuel supplied, the increase of $F(a, b, T)$ for given a, b, T shows that actually the width of the reaction zone in the flame, in which simultaneous $a \neq 0$, $b \neq 0$ exists, decreases while the magnitudes of a and b decrease.

In the limit for infinitely rapid reaction, a and b in the reaction zone approach zero so that nowhere (except for an infinitely narrow zone) can a and b simultaneously differ from zero. Thus in the case of combustion, by finding the distribution of p in space from the solution of linear equation (15) with conditions (16), the field of a and the field of b are found:

$$\left.\begin{aligned} p > 0,\ a = \frac{p}{\alpha},\ b = 0 \\ p < 0,\ a = 0,\ b = -\frac{p}{\beta} \end{aligned}\right\} \qquad (17)$$

The condition $p = 0$ also represents the equation of the surface of the flame. It is not difficult to show that the flow of the substance a reaching this surface on one side and of the substance b reaching it on the other side are precisely in stoichiometric ratio. At the flame surface, $p = a = b = 0$ so that the convective parts of the flow $\rho a\vec{w}$, $\rho b\vec{w}$, and $\rho p\vec{w}$ are identically equal to zero. Therefore on the surface

$$\left.\begin{aligned} \vec{q}_a &= \rho D \operatorname{grad} a = \frac{1}{\alpha} \rho D \operatorname{grad} p \\ \vec{q}_b &= \rho D \operatorname{grad} b = \frac{1}{\beta} \rho D \operatorname{grad} p \end{aligned}\right\} \tag{17a}$$

and the magnitude grad p has no singularity on the flame surface where $p = 0$, for on this surface the value of F in the equation for a and b is large but that in the equation for p is not.

The flame surface ($p = 0$) was found by Burke and Schumann by integrating equation (15) for the simplest case of concentrated flows of fuel and air moving with equal velocity. Their results are in agreement with experiment.

An attempt is made here to express the equations for the temperatures and the products of combustion in terms of a and b.

By considering the equation for one definite product of combustion

$$L(\gamma g) = F$$

and comparing it with the equation for a and b

$$L(\alpha a) = -F$$

$$L(\beta b) = -F$$

it can be seen that F can be eliminated from the equation by various methods. In order to obtain also the simplest boundary conditions, however, it is necessary to choose a new variable in an entirely definite manner:

$$r = \frac{a}{a_0} + \frac{b}{b_0} + \gamma g\left(\frac{1}{\alpha a_0} + \frac{1}{\beta b_0}\right)^2 \qquad {}^{1}(18)$$

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[1] Any combination $z = n\ (\gamma g + m\alpha a + (1-m)\beta b)$ where n and m are any constants gives $L = n\ \boxed{F-mF-(1-m)F} \equiv 0$. However, in order that z should have the same values for $a = a_0$, $b = 0$ and for $a = 0$, $b = b_0$, it is necessary that $nm\alpha a_0 = n(1-m)\beta b_0 = 1$, which leads to the given expression for r (equation (18)).

It is then easy to show that

$$\left.\begin{aligned} & & L(r) &= 0 \\ &\text{I)} & r &= 1 \\ &\text{II)} & r &= 1 \end{aligned}\right\} \qquad (19)$$

3. DISTRIBUTION OF PRODUCTS OF REACTION AND OF TEMPERATURE

From equation (18) and conditions (19), it is seen that in the entire region r satisfies the equation of diffusion and of convective transfer without sources or sinks (because the right side of the equation is equal to zero); r is so chosen that $r = 1$ in all flows reaching the region considered both in the flow of the gas (I) and in the flow of the air or atmosphere (II). It is evident that if in the two intermixing flows some substance (r) is contained in the same concentration, the same constant concentration will hold in the entire region of mixing. Mathematically, this condition is expressed such that $r \equiv 1$ is the solution of equations (18) and (19). From this solution the expression of g is found in terms of a and b

$$g = \frac{\alpha\beta}{\gamma} \frac{a_0 b_0 - ab_0 - a_0 b}{\alpha a_0 + \beta b_0} \qquad (20)$$

and entirely analogous expressions for h or T are obtained by replacing γ by η or τ. The proposed problem is thus solved.

In a rapid combustion when equations (17) are satisfied, on the flame front $(p = 0,\ a = b = 0)$

$$g_{00} = \frac{\alpha\beta}{\gamma} \frac{a_0 b_0}{\alpha a_0 + \beta b_0} \qquad (21)$$

This result has a very simple and clear physical meaning: The magnitudes a_0 and b_0 characterize the concentrations of the active substances in the burning gases. In order to obtain a stoichiometric mixture in which 1 gram is to react, it is necessary to take $1/\alpha$ grams of the substance a and $1/\beta$ grams of the substance b; there is then obtained $1/\gamma$ grams of the substance g. Because the substances a and b in the initial gases are diluted, it is necessary to take $1/\alpha a_0$ of one gas and $1/\beta b_0$ of the other. After combustion, a quantity $1/\gamma$ of the substance g will be contained in the total quantity of the products of combustion equal to

$$\frac{1}{\alpha a_0} + \frac{1}{\beta b_0}$$

which will give the concentration g_{00} satisfying equation (21).

In this way, for a rapid combustion of the unmixed gases in the reaction zone there is obtained accurately the same concentration of the products of combustion as though the burning gases were mixed in the stoichiometric ratio and the chemical reaction conducted without any diffusion exchange.

In exactly the same manner, in the absence of the heat losses by radiation and of the cooling surfaces in the flame and for equality of the coefficient of temperature conductivity and diffusion it may be shown that the temperature in the combustion zone of a diffused flame $T_{00} = \frac{\alpha\beta}{\tau} \frac{a_0 b_0}{\alpha a_0 + \beta b_0}$ is identically equal to the temperature of the combustion constant pressure of the stoichiometric mixture of the gases considered.

4. COMPARISON OF FLAME TEMPERATURE WITH TEST VALUES

The conclusion that the temperature of an unmixed flame is equal to the temperature of combustion of the stoichiometric mixture is in contradiction to test results. It is well known from daily laboratory tests that in the combustion of a given illuminating gas in a Bunsen burner with closed air intakes the temperature of the flame is lower than in the case where the same gas burns with the intakes left open, so that a prepared mixture of gas and air reaches the flame. [2]

This divergence from test results is explained not by an error in the computation but by the fact that the initially imposed condition of applicability of the computation, which is that in the heat balance of the laboratory burner the amount of heat given off by radiation must not be neglected, was not satisfied.

For an equal quantity of burning gas, that is, for an equal amount of heat given out without the supply of air, the dimension of the flame

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[2] It is assumed here and in the following discussion that a stoichiometric quantity of air is drawn in. It is possible to consider the case of an insufficient quantity when two flame cones are formed, an inner (compressible mixture) and an outer (complete burning in the surrounding air).

is considerably greater than with the supply of air so that the radiating surface is greater and the amount of chemical energy given out per unit surface is less. In addition, the luminosity of the flame without air supply is greater on account of the occurrence in it of minute particles of carbon arising from the decomposition of the hydrocarbons of the fuel. When air is supplied, the carbon soot disappears. The presence of soot in the flame of a mixed gas is entirely natural from the following considerations: Consider point A in the steady-state region (fig. 1), that is, within the flame surface. Let this point be near the surface of the flame. In this case the temperature at point A is high, the gas is already strongly diluted with the products of combustion and with nitrogen, but there is no oxygen in it. Heating in the absence of oxygen leads to the formation of soot particles.

In a flame of a mixture of gas and air, the gas is heated ahead of the flame front, but this heating occurs in the presence of oxygen and the particles of carbon molecules that might act as initial centers for the formation of soot particles are all oxidized. As a result, the heat radiation from the flame of the mixture is considerably lower than in the flame of the unmixed gas, although the initial "ideal" theoretical value of the combustion temperature in both cases is the same. As has already been shown, this theoretical value represents the temperature that must prevail during combustion in the absence of losses by radiation and side reactions and with full account taken of the conductive and convective heat interchange of the flame with the gas and air.

Account of the conductive and convective heat interchange is fundamentally required for this heat interchange is directly connected with those processes that supply the fuel and the oxygen to the flame. No matter in what ratio the available and supplied air and gas exist when they are individually supplied, the flame establishes itself in such position that the fuel and the oxygen reach the surface in the stoichiometric ratio. For equal coefficients of diffusion and temperature conductivity (particularly in turbulent motion, assuring such equality), the concentration of the products of combustion and the temperature of the flame correspond precisely to the combustion of a stoichiometric mixture (for equal losses by radiation). Such is the conclusion from the theory.

5. LIMIT OF COMBUSTION OF UNPREMIXED GASES

The method described permits computing the position of the surface of the flame for the supply of any amount of gas and air for any small calorie content of the gas. This computation is based on the assumption of a high rate of chemical reaction at the flame surface (and at the temperature of combustion) that leads to a small thickness of the zone in which the chemical reaction proceeds and to the possibility of considering the flame as a geometrical surface.

It is evident that for an insufficiently large rate of chemical reaction a deviation from this picture is to be expected. By analogy with other phenomena of combustion and explosion, it may be expected that a decrease in the rate of reaction for otherwise equal conditions effects at first only a certain quantitative change - a widening of the zone of reaction. After the attainment of a certain critical value, an extinction of the flame occurs, the combustion becoming impossible, and instead of the flame there occurs a mixing of the cold gas and air without any reaction. An attempt is made to consider the critical conditions of extinction in the simplest schematized case.

In 1940, this author considered (reference 3) the conditions of the possible combustion (flame propagation) in a prepared mixture of gases. In this case the limit depended on the lowering of the temperature of combustion because of the heat transfer to the side walls of the pipe and heat loss by radiation. The lowering of the temperature of combustion in turn led to the decrease in the velocity of flame propagation, that is, to the decrease in the amount of heat given out per second. With a decrease in the velocity of the flame, the relative heat losses increase and so forth. For this reason it was possible to write down the critical condition of the possibility of combustion of a prepared mixture such that the lowering of the temperature of combustion because of the effects of the heat losses must not exceed a certain small limit (RT_c^2/A, where A is the heat of activation of the combustion reaction and T_c is the combustion temperature).

This theory of the effects of external heat losses is not applicable to the combustion of unmixed gases. The lowering of the temperature of combustion in this case does not lead to a change in the amount of gas burning per unit surface of the flame, because the rate of combustion is here determined exclusively by the rate of the diffused oxygen and fuel supplied to the flame surface and not by the velocity of propagation (depending on the rate of reaction) as was the case for a prepared mixture.

The limit of combustion of unmixed gases is determined by the lowering of the temperature that depends on the finite velocity of the chemical reaction.

Consider the distribution of the concentrations and the temperature in the reaction zone. If the rate of reaction were infinite, the distribution would be given by figure 2. The dotted line shows the position of the zone in which $a = 0$, $b = 0$. This line is taken as the origin for computing the coordinate x, which is taken perpendicular to the flame surface. If the total amount of substance reacting on unit surface in unit time is denoted by M, the diffusion flows a and b are respectively equal to[3]

$$\left.\begin{aligned} -\rho D \frac{\partial a}{\partial x} &= \frac{1}{\alpha} \frac{M}{\frac{1}{\alpha} + \frac{1}{\beta}} = \frac{\beta}{\alpha + \beta} M \\ \rho D \frac{\partial b}{\partial x} &= \frac{\alpha}{\alpha + \beta} M \end{aligned}\right\} \qquad (22)$$

so that the distribution of the reacting components near the zone is given by the formulas

$$\left.\begin{aligned} x < 0 \qquad a &= \frac{M}{\rho D} \frac{\beta}{\alpha + \beta} (-x) \qquad b = 0 \\ x > 0 \qquad a &= 0 \qquad b = \frac{M}{\rho D} \frac{\alpha}{\alpha + \beta} x \end{aligned}\right\} \qquad (23)$$

With the aid of equations (20) and (21) rewritten for T, the corresponding temperature distribution is obtained. In the general case

$$\left.\begin{aligned} T &= T_{00}\left(1 - \frac{a}{a_0} - \frac{b}{b_0}\right) \\ \text{where} \qquad T_{00} &= \frac{\alpha\beta}{\tau} \frac{a_0 b_0}{\alpha a_0 + \beta b_0} \end{aligned}\right\} \qquad (24)^4$$

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[3] Because the neighborhood of the reaction zone is considered, ρ and D in these formulas and those following must be taken at the temperature in the reaction zone, approximately at T_{00}.

[4] More accurately $T_{00} = \frac{\alpha\beta}{\tau} \frac{a_0 b_0}{\alpha a_0 + \beta b_0} + T_0$. In the following discussion the initial temperature T_0 is small in comparison with the temperature of combustion and shall be neglected throughout.

Substition of the expressions for a and b in equations (23) gives

$$\left.\begin{aligned} T &= T_{00}\left(1 - \frac{1}{a_0}\frac{M}{\rho D}\frac{\beta}{\alpha + \beta}(-x)\right) \qquad x < 0 \\ T &= T_{00}\left(1 - \frac{1}{b_0}\frac{M}{\rho D}\frac{\alpha}{\alpha + \beta}\,x\right) \qquad x > 0 \end{aligned}\right\} \tag{25}$$

The corresponding curve is also shown in figure 2.

Consider how the curves vary in the case where the reaction is not instantaneous.

It is evident that for equal amount of substance burning per unit surface M, the gradient of the concentration and the entire distribution of a and b far from the zone do not change. The curves a and b now cannot, however, undergo a sharp break (correspnding to the instantaneous reaction) at the origin of coordinates as in figure 2. They will curve as is shown in figure 3, approaching zero asymptotically in the region occupied by the second component. The dotted line on this figure shows the distribution for the instantaneous reaction.

In order to find accurately the curve of the concentration distribution (fig. 3), it is necessary to integrate the equations of diffusion of the form of equations (12), substituting a definite expression for the rate of chemical reaction; for example,

$$F = abKe^{-\frac{E}{RT}} \tag{26}$$

Because F depends on at least the three magnitudes a, b, and T, it is necessary to consider a system of three equations of the second order. On account of the devices developed, it is possible first to find p, connecting a and b, and then express T in terms of a and b and thus reduce the problem to a single equation of the second order; for example, for a in which F will be expressed in terms of a and the known function p(x).

For present purposes, however, this method is too complicated and the conclusions of interest can be obtained (with an accuracy up to an unknown numerical factor) by the methods of dimensional analysis and the theory of similarity.

The following effective magnitudes are introduced: the width of the zone x_1, the temperature in the reaction zone T_1, and the concentrations a_1 and b_1. The total amount of substance reacting in the entire zone is expressed in terms of these effective magnitudes:

$$M = a_1 b_1 K x_1 e^{-\frac{E}{RT_1}} \tag{27}$$

Everything is expressed on the right-hand side in terms of x_1. In order to interconnect these terms, it is noted that the dependence of a and b on x is given at the distances from the zone, which are large in comparison with the width of the reaction zone x_1. The dependence is a linear one, that is, characterized by the given gradients $\partial a/\partial x$, $\partial b/\partial x$ or by the ratios a/x, b/x (See equations (23)[5]). From the dimensions, it is seen that the relation between a_1, b_1, and x_1 must be given by the same equations

$$\left.\begin{aligned} a_1 &= \frac{M}{\rho D} \frac{\beta}{\alpha + \beta} x_1 \\ b_1 &= \frac{M}{\rho D} \frac{\alpha}{\alpha + \beta} x_1 \end{aligned}\right\} \tag{28}$$

The relation between T_1, a_1, and b_1 is given by equations (24), from which, on substitution of equations (28),

$$T_1 = T_{00} (1-\varphi M x_1)$$

where

$$\varphi = \frac{1}{\rho D} \frac{\frac{\beta}{a_0} + \frac{\alpha}{b_0}}{\alpha + \beta} = \frac{\alpha\beta}{\alpha + \beta} \frac{1}{\rho D T_{00}} \tag{29}$$

is obtained.

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[5] The ratios a/x and b/x change little only at distances greater than x_1 but less than the dimensions of the flame. At distances comparable with the flame dimensions, the convective terms in the diffusion equation must not be neglected.

Substitution in equation (27) gives an equation connecting M and x_1:

$$\left.\begin{aligned} M &= \frac{\alpha\beta}{(\alpha+\beta)^2}\,\frac{M^2}{(\rho D)^2}\,Kx_1^{\,3}\exp\left(-\frac{E}{RT_{00}(1-\varphi M x_1)}\right) \approx \\ &\frac{\alpha\beta}{(\alpha+\beta)^2}\,\frac{M^2}{(\rho D)^2}\,Ke^{-\frac{E}{RT_{00}}}\,x_1^{\,3}\,e^{-\frac{\varphi M x_1 E}{RT_{00}}} \end{aligned}\right\} \qquad (30)$$

In the second line of equation (30), the magnitude in the exponent is expanded in a series by the method of Frank-Kamenetskii (reference 4). The magnitude on the right side depending on x_1 has the form x^3e^{-mx} and therefore passes through a maximum for a definite critical value $x_1 = x_{cr}$:

$$x_{cr} = \frac{3RT_{00}}{\varphi ME} \qquad (31)$$

$$M_{cr}^{\,2} = \frac{\alpha\beta}{(\alpha+\beta)^2}\left(\frac{RT_{00}}{E}\right)^3 \rho D\left(\frac{\alpha+\beta}{\frac{\beta}{a_0}+\frac{\alpha}{b_0}}\right)^3 Ke^{-\frac{E}{RT_{00}}} \qquad (32)$$

The significance of the maximum M as a function of x_1 lies in the fact that for small x_1, the overlapping of a and b is small, the reaction zone is narrow, and the concentrations of the reacting substances in it are small.

For small x_1 and given temperature T_{00}, the temperature T differs little from T_{00}, $M \sim x_1^{\,3}$, and $a_1 \sim b_1 \sim x_1 \sim \sqrt[3]{M}$ corresponding to well-known results for cold diffusion flames in a high vacuum (reference 5). For large x_1, the concentrations of the reacting substances are large; the temperature, however, is lowered, leading to a decrease in the total amount of reacting substance.

On intensifying the combustion by increasing the supply of reacting substances a and b to the zone, the cooling of the reaction zone is simultaneously increased. Until the rate of reaction is sufficiently large, x_1 is less than the maximum and the temperature is practically not lowered. For a certain critical value M_{cr}, however (formula (32)), a lowering of the temperature of the zone is obtained, leading to a further decrease in the rate of reaction and a further lowering of the temperature. A breakoff of the combustion occurs and instead of the combustion there is a mixing of the cold gases. The maximum possible lowering of the temperature (before flame extinction) is equal to $3RT_{00}^2/E$. There is an interesting resemblance of the expression for M_{cr} (equation (32)) to the expression for the amount of substance burning per unit time in the flame propagated for a previously prepared stoichiometric mixture of a combustible gas with air, the burning of which in the unmixed form was previously considered.

Following the work of Frank-Kamenetskii and the author there is obtained for the propagation of a flame in a stoichiometric mixture (reference 6) in the notation here assumed

$$M_{mix}^2 = \frac{(\alpha\beta)^2}{\left(\frac{\beta}{a_0} + \frac{\alpha}{b_0}\right)^3}\left(\frac{RT_{00}}{E}\right)^3 6\rho DKe^{-\frac{E}{RT_{00}}} \tag{33}$$

which differs from equation (32) only by the factor $6\alpha\beta/(\alpha + \beta)$, which has no significance because numerical multipliers were omitted in the derivation of equation (32). This agreement is very interesting from the fundamental point of view for it shows that the maximum intensity of combustion of a mixture and unmixed gases, if the mixing is sufficiently intensified, is of the same order.

In the theory of combustion of an explosive mixture, it has been shown that the chemical reaction proceeds in the zone in which the concentration of the reacting gas (of the one that is insufficient in the mixture or of both in the case of a stoichiometric mixture) is very small, of the order of RT_{00}/E of the initial concentration. As the computations showed, for the combustion of unmixed gases the concentrations of both reacting substances (fuel and oxygen) in the reaction zone are very small. These concentrations depend on the intensity of the combustion; in contrast to an explosive mixture for which there is a characteristic magnitude of intensity of combustion (velocity of the flame), the intensity of the combustion of the flame of unmixed gases M depends on external conditions. For maximum possible M at the limit of breakoff of the flame, however, the concentrations in the reaction zone do not exceed the order of magnitude of the fraction RT_{00}/E of the concentrations in the stoichiometric mixture.

The limit found for the intensity of combustion of unmixed gases explains, at least qualitatively, the fact that in the flow of a rapid stream out of a pipe the flame is entirely situated at a certain distance from the exit section of the pipe so that at the exit, where the intermixing of the reacting substances is most intense, the flame breaks away. The losses by radiation have not been taken into account. In taking them into account, it is evidently necessary to substitute in equations (29) to (32) in place of the theoretical value T_{00}, computed from the specific heat, the maximum possible temperature T'_{00} for instantaneous reaction with account taken of the radiation. The temperature T'_{00} is less than T_{00} even for an infinitely thin zone as $x_1 \longrightarrow 0$ on account of the radiation of the heated gases on the left and right of the reaction zone. The temperature T'_{00} is lowered with the value of M because for small M less heat is given off and the radiating zone is wider. For a lowering of M due to the decrease in T'_{00} with radiation taken into account, there will also be a decrease in M_{cr} (equation (32)) and for very small M there arises the second lower limit of M, that is, the breaking off of the flame for too small an intensity of the combustion. Finally, for a small calorific value of the gas the upper and lower limits of M may coincide and the combustion become entirely impossible. Qualitatively, the picture is analogous to the more simple case of the exothermic reaction in a jet with account taken of the heat transfer, a case considered by Zysin and the author (reference 7).

In the present report, the practically important but more complicated question of the limit of intensification of the turbulent combustion of unmixed gases is not considered. The complexity of this problem is connected with the fact that in the presence of turbulence connecting the mean rate of reaction with the mean temperature is not justified. It is here evidently necessary to determine experimentally the limits of the possible conditions of combustion.

With the aid of equations (12) with a definite form of the function F (for example equation (26)), it is also possible to solve the important interesting problem of the diffusion passage of the fuel through the flame zone; as is shown in figure 3, the concentration of the interpenetrating reacting substances drops sharply in passing through the reaction zone but does not become zero. Because the temperature and the rate of reaction likewise drop on both sides of the reaction zone, the concentration of the fuel that has already reached a definite distance from the flame in the oxidizing zone does not further vary. The method presented is unsuitable for solving this problem, however, and it is necessary to solve the equations as described in the text after equation (26).

CONCLUSIONS

The distribution of the concentrations of the products of combustion and the temperature for the combustion of initially unmixed gases were considered. It was shown that for the simplest assumptions these concentrations and the temperature at the flame surface are the same as for the combustion of an initially prepared stoichiometric mixture of the gases considered.

The possible limit of the intensification of the combustion of unmixed gases, which depends on the finite rate of the chemical reaction, was obtained. In order of magnitude, this limit is near the rate of combustion of a stoichiometric mixture.

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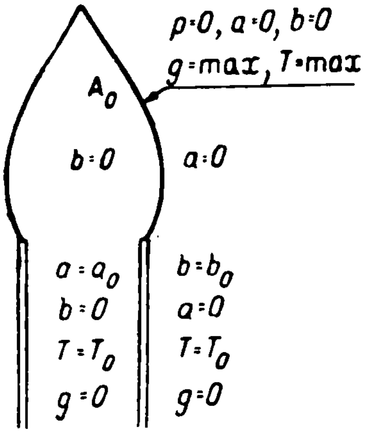

Figure 1.

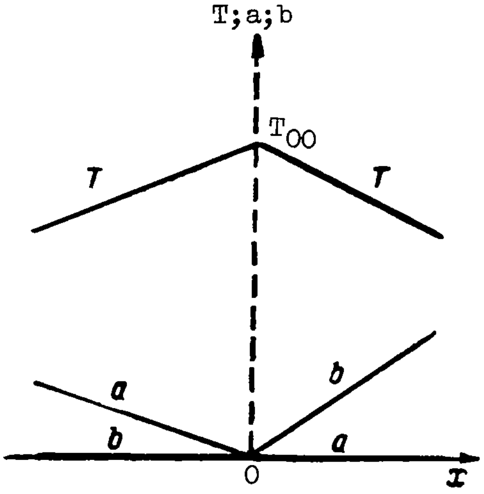

Figure 2.

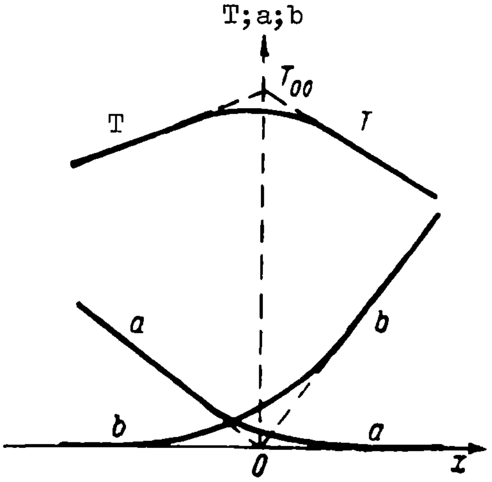

Figure 3.

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