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dedicated to C. B. Biezeno

*by some of his friends and former students
on the occasion of his
sixty-fifth birthday*

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The thermal theory
of constant pressure deflagration

1. The fundamental problem of the theory of combustion consists in the computation of the so called normal velocity of combustion, i.e. the velocity of propagation of a combustion wave in a gas mixture, which is capable of a well defined chemical reaction. Instead of investigating the propagation of the combustion process in the gas mixture at rest one can consider stationary flow relative to a combustion or flame front, which is fixed in space. We assume that the gas is infinitely extended in space and the flame front is perpendicular to the x-axis, so that temperature, density, chemical composition and velocity are functions of the x-coordinate only. For a great class of combustion processes laminar flow can be assumed and it can be shown that the assumption of constant pressure gives a fair approximation [1]). Also viscous forces can be neglected. According to a full analysis of the combustion process two physical phenomena are responsible to carry the combustion ahead through the gas mass: heat transfer and transfer of matter, especially. transfer of active radicals from the zone where intensive chemical reaction takes place to the domain filled by the unburned gas mixture. The thermal theory considers heat transfer only and neglects diffusion. Although this means a considerable restriction, the thermal theory gives a fair description of the phenomena and many of its predictions are confirmed by experiment.

2. Three equations express the principles of conservation of matter, momentum and energy. Under the simplifying assumptions given above, the three equations read

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1) Compare e.g. v. KÁRMÁN, Proceedings of the First U.S. National Congress for Applied Mechanics (Chicago, June 1951, to be published 1952).

$$\varrho v = m \tag{1}$$

$$p = p_o \tag{2}$$

$$mH - \lambda \frac{dT}{dx} = mH_o \tag{3}$$

where p, ϱ, T and v are the pressure, density, temperature and velocity of the gas mixture, at an arbitrary point. H denotes the total (thermodynamic + chemical) enthalpy, and λ the coefficient of heat transfer. The constants m, p_o and H_o are respectively the mass flow in unit time through a unit cross section normal to the x-direction, the pressure assumed to be constant in the whole space and the initial value of the total enthalpy of the gas mixture.

Concerning the chemical reaction we assume:

a) that the change of the number of molecules in the unit mass due to the chemical reaction can be neglected. This assumption is not essential from the viewpoint of the theory and is made mainly for the reduction of numerical computations. If we make this assumption the equation of state can be written in the form $p/\varrho = R_g T$, whatever the chemical composition may be; R_g is the gas constant of the unburned mixture.

b) that the chemical reaction can be described by one parameter ε, such that the chemical energy of the unit mass of the mixture in an arbitrary intermediary state can be written in the form $(1 - \varepsilon) E_o + \varepsilon E_f$, where E_o is the energy of formation of the initial and E_f is that of the final products. It is seen that ε is a measure of the fraction of the reaction, which has been completed. If $E_o - E_f = q$ is called the heat released by unit mass due to the reaction, it is evident that $q\varepsilon$ plays the role of heat introduced between the initial state and the state corresponding to the value ε of the chemical parameter. Therefore eq. (3) can be written in the form

$$mh - \lambda \frac{dT}{dx} - mq\varepsilon = mh_o, \tag{3a}$$

where h and h_o are the values of $h = \int_0^T C_p dT$ and $h_o = \int_0^{T_o} C_p dT$ respectively, T_o being the temperature in the initial state and C_p the specific heat of the mixture at constant pressure.

For simplicity's sake for the following computations both C_p and λ will be replaced by constant mean values.

The three equations together with the equation of state would determine p, ϱ, T and v if the chemical parameter ε is given. Evidently in order to solve our problem we have to state the interconnection of ε with the physical parameters p, ϱ, T and v. This statement has to come from chemical kinetics. First if diffusion is neglected our chemical parameter is connected with the "rate of reaction" w by the relation

$$\varrho \frac{d\varepsilon}{dt} = w \qquad (4)$$

or in the specific case of stationary flow

$$\varrho v \frac{d\varepsilon}{dx} = m \frac{d\varepsilon}{dx} = w. \qquad (4a)$$

Chemical kinetics states that w is a given function of p_o, T and ε, so that the relation

$$m \frac{d\varepsilon}{dx} = w \, (p_o, T, \varepsilon) \qquad (4b)$$

completes the system of equations to be solved.

3. The solution we are seeking to establish has to satisfy in the entire space $-\infty < x < \infty$ the equations (1), (2), (3a), and (4b) with the following boundary conditions:

for $\quad x = -\infty \quad T = T_o, \quad \dfrac{dT}{dx} = 0, \quad \varepsilon = 0;$

for $\quad x = \infty \quad T = T_f, \quad \dfrac{dT}{dx} = 0, \quad \varepsilon = 1.$

The symbol T_f denotes the final value of the temperature T. Due to eq. (3a), with the constant value of C_p,

$$q = C_p \, (T_f - T_o) \qquad (5)$$

and therefore equation (3a) can be written also in the form

$$\lambda \frac{dT}{dx} = mC_p \left[T - T_o - \varepsilon \, (T_f - T_o) \right] \qquad (6)$$

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Combining this equation with (4b) one has

$$\frac{\lambda}{m^2 C_D} \, w \, \frac{dT}{d\varepsilon} = T - T_o - \varepsilon \, (T_f - T_o) \tag{7}$$

According to what chemical kinetics is teaching, the rate of reaction w for $\varepsilon = 0$ is positive for all values of the temperature. It disappears only when $T \to 0$. Hence there cannot exist a solution of equation (7) for which $\varepsilon \to 0$ and $T \to T_o$, provided the relation between w and T is valid in the whole domain $T_o \leqq T \leqq T_f$. Physically speaking there must be a range $-\infty < x < x_i$ in which the reaction does not take place according to the rate of reaction given by the simple rules of chemical kinetics; when the temperature T is inferior to an "ignition temperature" $T_i = T(x_i)$ the gas mixture is well capable to undergo a chemical reaction but the reaction fails to realize. At this stage of the analysis we want only to state that we are forced to such an assumption provided we are sure that a combustion wave with constant velocity of propagation and unchanged temperature distribution exists. At the end of the paper we want to make some further remarks on the physical meaning of the assumption of an ignition temperature.

4. The commonly used relation for the rate of reaction can be written in the form

$$w = \frac{K p_o{}^n}{R_g{}^n \, \varrho_s{}^{n-1}} \cdot \frac{(1 - \varepsilon)^n}{T^n} e^{-\frac{A}{RT}} \tag{8}$$

where K is a constant which has the dimension of the reciprocal of a time, and ϱ_s is a density of reference. The energy A is called the activation energy.

The exponent n is in general an integer which designates the order or "molecularity" of the reaction (mostly $n = 1$ or 2).

We assume equation (8) is valid for $T \geqq T_i$, whereas $w = 0$ for $T_o \leqq T < T_i$.

Then our problem consists of two parts:

a) For $T < T_i$ we have to integrate the differential equation

$$\lambda \frac{dT}{dx} = n C_D \, (T - T_o) \tag{9}$$

with the boundary conditions

$$x = -\infty \qquad T = T_o \atop x = x_i \qquad T = T_i \Bigg\} \tag{10}$$

b) For $T > T_i$ we have to integrate the differential equation:

$$\frac{\lambda K p_n{}^n}{m^2 C_p R_g{}^n \varrho_s{}^{n-1} T_f{}^n} \left(\frac{T_f}{T}\right)^n (1 - \varepsilon)^n\, e^{-\frac{A}{RT}} \frac{dT}{d\varepsilon} = T - T_o - \varepsilon(T_f - T_o), \tag{11}$$

with the boundary conditions

$$\varepsilon = 0, \qquad T = T_i, \atop \varepsilon = 1, \qquad T = T_f \Bigg\} \tag{12}$$

5. It is seen that equation (11) is an ordinary differential equation of the first order for $T\,(\varepsilon)$ where T has to satisfy boundary conditions at each end of the interval $0 \leqq \varepsilon \leqq 1$. Therefore we have to solve an "eigenvalue" problem. Evidently the only parameter which is not given by the statement of the problem is the massflow m. We have to determine the value of m for which T can satisfy both conditions (12). Denoting this value of m by m_o, $\varphi = \dfrac{m_o}{\varrho_o}$ will be the normal combustion velocity, which evidently depends on p_o, T_f and the assumed ignition temperature T_i.

When the value of the parameter m is determined, the equations (9) determine uniquely T as function of x for $T < T_i$. This zone is called the "heating zone". The zone $x > x_i$ can be called the "reaction zone". The reason for this terminology is self explanatory. Evidently heat transfer from the reaction zone to the heating zone serves to elevate the temperature of the gas in front of the flamefront to the ignition limit.

It is seen from equations (11) that if we use the form of law for the rate of reaction given by (8), the governing parameter is

$$A = \frac{\lambda}{m^2 C_p} \frac{K p_o{}^n}{R_g{}^n \varrho_s{}^{n-1} T_f{}^n} = \frac{\lambda K \varrho_o}{m^2 C_p} \left(\frac{T_o}{T_f}\right)^n \left(\frac{\varrho_o}{\varrho_s}\right)^{n-1}. \tag{13}$$

Therefore it can be stated that the expression for the normal combustion velocity φ must have the form:

$$\varphi = \sqrt{\frac{\lambda K}{\varrho_0 C_p} \left(\frac{\varrho_0}{\varrho_s}\right)^{n-1} \left(\frac{T_0}{T_f}\right)^n} \cdot f\left(\frac{A}{RT_f}, \frac{T_0}{T_f}, \frac{T_i}{T_f}\right). \tag{14}$$

In the following section an example of approximate solution is given for a first order reaction $(n = 1)$. The method of approximation is based on the peculiar behavior of the exponential function $e^{-\frac{A}{RT}}$ which has been first introduced by Arrhenius into the theory of rate of reaction.

6. First we want to introduce some notations for simplification of the computations.

The parameter A is defined as

$$A = \frac{\lambda K \varrho_0}{m^2 C_p} \left(\frac{T_0}{T_f}\right). \tag{15}$$

We introduce the nondimensional parameters

$$\theta = \frac{T}{T_f}, \quad \theta_a = \frac{A}{RT_f}. \tag{16}$$

The values of θ for $T = T_0$ and $T = T_i$ will be denoted by θ_0 and θ_i respectively.

For $n = 1$, we have from Eq. (11)

$$A \frac{1-\varepsilon}{\theta} e^{-\frac{\theta_a}{\theta}} \frac{d\theta}{d\varepsilon} = \theta - 1 + (1 - \theta_0)(1 - \varepsilon). \tag{17}$$

It is seen that Eq. (17) has a singular point at $\varepsilon = 1$, $\theta = 1$. The solution near this point must satisfy the condition

$$1 - \theta \approx \frac{1 - \theta_0}{1 + Ae^{-\theta_a}}(1 - \varepsilon). \tag{18}$$

This condition fixes the tangent of the $\theta(\varepsilon)$ curve at $\theta = 1$, $\varepsilon = 1$ as function of A.

The idea of our approximation is to considerer two domains, one near $\varepsilon = 1$ and another one near $\varepsilon = 0$ [1]).

a) In the domain near $\varepsilon = 1$ the expression (18) is considered as fair approximation to be substituted for $\theta - 1$ on the right side

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1) J. CORNER and S. F. BOYS use an iteration-method starting from the solution valid near $T = T_f$ (Proc. Roy. Soc. London, Vol. 197 (1949) p. 90—108).

of Eq. (17). Then Eq. (17) can be solved by quadrature and one obtains with $\varepsilon = 1$ for $\theta = 1$:

$$1 - \varepsilon = \frac{1 + Ae^{-\theta_a}}{(1 - \theta_o)\, e^{-\theta_a}} \int\limits_{\theta}^{1} \frac{e^{-\frac{\theta_a}{\theta}}}{\theta}\, d\theta. \tag{19}$$

b) Near $\varepsilon = 0$ we approximate Eq. (17) by

$$A\, \frac{e^{-\frac{\theta_a}{\theta}}}{\theta}\, \frac{d\theta}{d\varepsilon} = \theta - \theta_a, \tag{20}$$

from which it follows, with $\varepsilon = 0$ for $\theta = \theta_i$:

$$\varepsilon = A \int\limits_{\theta_i}^{\theta} \frac{e^{-\frac{\theta_a}{\theta}}}{\theta\,(\theta - \theta_o)}\, d\theta. \tag{21}$$

It is supposed that the expression (19) is valid between a "transition temperature" θ_t and $\theta = 1$, whereas the expression (21) is valid between $\theta = \theta_i$ and $\theta = \theta_t$. The value of θ_t is determined in such a way that ε and $\dfrac{d\varepsilon}{d\theta}$ are continous at the point of transition. These conditions of continuity yield the equations

$$1 = A \int\limits_{\theta_i}^{\theta_t} \frac{e^{-\frac{\theta_a}{\theta}}}{\theta\,(\theta - \theta_o)}\, d\theta + \frac{1 + Ae^{-\theta_a}}{1 - \theta_o}\, e^{\theta_a} \int\limits_{\theta_t}^{1} \frac{e^{-\frac{\theta_a}{\theta}}}{\theta}\, d\theta, \tag{22}$$

$$\frac{1 + Ae^{-\theta_a}}{(1 - \theta_o)\, e^{-\theta_a}} = \frac{A}{\theta_t - \theta_o}, \tag{23}$$

for the determination of θ_t and A. The Eq. (22) and (23) give the solution of our problem, since A determines the "eigenvalue" m_o of the massflow, i.e. the normal combustion velocity.

7. The solution of (22) and (23) involves rather elaborate numerical calculations. Since we did not have human, mechanical or electronic computers to our disposal, we introduced an approximation in the integral in the first term on the right side of Eq. (22), which is well justified with the exeption of the case, in which $\theta_i \to \theta_o$. Since the

exponential function $e^{-\frac{\theta_a}{\theta}}$ decreases very fast which decreasing values of the variable θ we write instead of

$$\frac{e^{-\frac{\theta_a}{\theta}}}{\theta\,(\theta - \theta_o)} \approx \frac{e^{-\frac{\theta_a}{\theta}}}{\theta\,(\theta_t - \theta_o)}.$$

Then the computation becomes rather simple, since by elimination of $\theta_t - \theta_o$ between (22) and (23) one obtains a single equation for Λ, which reads

$$1 = \frac{1 + \Lambda e^{-\theta_a}}{1 - \theta_o}\, e^{\theta_a} \int_{\theta_i}^{1} \frac{e^{-\frac{\theta_a}{\theta}}}{\theta}\, d\theta \tag{24}$$

The integral

$$\int_{\theta_i}^{1} \frac{e^{-\frac{\theta_a}{\theta}}}{\theta}\, d\theta = E_i\left(-\frac{\theta_a}{\theta_i}\right) - E_i\left(-\theta_a\right).$$

The function E_i is tabulated. Then we have

$$\Lambda = e^{\theta_a}\left\{ \frac{1 - \theta_o}{e^{\theta_a}\left[E_i\left(-\frac{\theta_a}{\theta_i}\right) - E_i\left(-\theta_a\right)\right]} - 1 \right\} \tag{25}$$

or from the definition of Λ (Eq. (15)):

$$\varphi^2 = \frac{\lambda K \theta_o}{\varrho_o C_p} \frac{e^{-\theta_a}}{\dfrac{1 - \theta_o}{e^{\theta_a}\left[E_i\left(-\frac{\theta_a}{\theta_i}\right) - E_i\left(-\theta_a\right)\right]} - 1} \tag{26}$$

Also, one obtains from Eq. (19), by substituting the value of Λ from Eq. (25) an explicit expression for ε as function of θ, valid for $\theta_t < \theta < 1$:

$$\varepsilon = \frac{E_i\left(-\frac{\theta_a}{\theta_i}\right) - E_i\left(-\frac{\theta_a}{\theta}\right)}{E_i\left(-\frac{\theta_a}{\theta_i}\right) - E_i\left(-\theta_a\right)}. \tag{27}$$

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If we use for the domain $\theta_i < \theta < \theta_t$ the same approximation for the computation of the function $\varepsilon = \varepsilon(\theta)$ which we used for the determination of Λ, Eq. (27) becomes a fair approximation for the whole domain between the ignition temperature θ_i and the final temperature $\theta_f = 1$.

Fig. 1 gives the computed values of

$$\frac{\varphi}{\sqrt{\dfrac{\lambda K \theta_o}{\varrho_o C_p} e^{-\theta_a}}}$$

as function of the ratio $\theta_i = T_i/T_f$ for the following choice of the activation energy and the T_o/T_f ratio: $\theta_a = 8$; $\theta_o = 0,15$.

One sees that for $\theta_i = 1$ $(T_i = T_f)$, $\varphi = 0$, as expected; between $\theta_i = 0,8$ and 1, the value of φ increases from zero to a value which remains almost constant until θ_i approaches θ_o. For $\theta_i \to \theta_o$, $\varphi \to \infty$. Our method of approximation is not valid for values of θ_i very close to θ_o. However the consideration of the ε vs θ curves, calculated for $\theta_i = 0,8$; 0,7 and 0,4 and given in Figure 2, leads to the conclusion that the change of φ from its almost constant value to infinity occurs in a very narrow range of θ_i, close to θ_o.

One sees from Figure 2 that the inclination of the tangent to the curve θ vs ε at $\varepsilon = 1$, $\theta = 1$ changes gradually from the horizontal
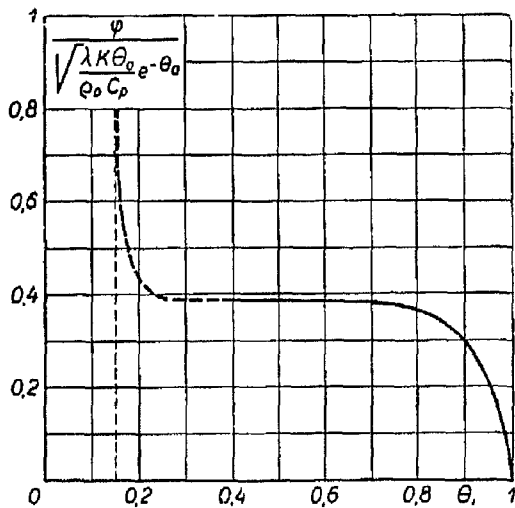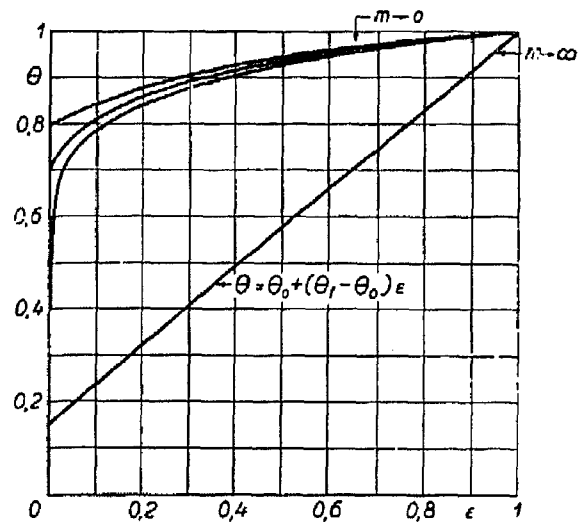
Fig. 1   Fig. 2

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direction which corresponds to $\varphi = 0$ to an angle of inclination which is almost independent of θ_i between $\theta_i = 0{,}8$ and $\theta_i = 0{,}4$. At the same time the inclination of the tangent at $\theta = \theta_i$ increases from the value $\left(\dfrac{d\theta}{d\varepsilon}\right)_{\varepsilon=0} = 0{,}51$ for $\theta_i = 0{,}8$ to $1{,}76$ for $\theta_i = 0{,}7$ and 2480 for $\theta_i = 0{,}4$.

This behaviour of the tangent at the lower cold end of the reaction zone is caused by the rapid increase of the value of $e^{\theta_a \frac{1-\theta_i}{\theta_i}}$ with decreassing θ_i. In fact we have

$$\left(\frac{d\theta}{d\varepsilon}\right)_{\varepsilon=0} = \frac{(\theta_i - \theta_a)\,\theta_i}{\Lambda e^{-\theta_a}}\,e^{\theta_a \frac{1-\theta_i}{\theta_i}}. \tag{28}$$

In this expression the denominator is almost constant, according to Fig. 1. Hence the exponential function in the numerator has the dominating influence, which prevails, till $\theta_i - \theta_o$ becomes very nearly equal to zero. If this occurs the curve θ vs ε which before was practically uninfluenced by the choice of θ_i, rapidly changes its shape and tends to approach the straight line $\theta = \theta_o + (1 - \theta_o)\,\varepsilon$ which is also shown in Figure 2. At the same time φ increases to infinity.

8. Tl e main conclusions of this investigation are, that

a) with the exception of the limiting case $\theta_i \to \theta_o$ the overwhelming bulk of the chemical reaction occurs at temperatures relatively near to the final temperature, practically independently of the choice of the ignition temperature [1]).

b) The mass flow i.e. the normal combustion velocity which makes the process stationary, is practically constant and independent of the choice of the ignition temperature, with the exception of a range near the final temperature (of the order of 20—25% of the whole interval between T_o and T_f) and a very close range near the initial temperature of the unburned gas mixture.

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1) N. Semenow (N.A.C.A. Techn. Mem. · 1026, 1084), Y. Zeldovich and D. A. Frank-Kamenetski (Acta phys. chim. U.S.S.R. 9 p. 341 and C.R. Acad. Sc. U.S.S.R.) recognized this fact and concluded that the ignition-temperature can be "eliminated" from the theory of the flame-velocity. The correct conclusion is given under *b*).

These conclusions may reconciliate the conscience of the chemist, who believes that the experimentally found ignition temperatures are not significant for the burning process in a combustion wave, and the conscience of the mathematicien, who believes that without defining a definite ignition temperature the problem is undetermined. However we are afraid that this reconciliation of the two different viewpoints is a rather superficial one. It remains as a serious problem, what physical or chemical process determines the beginning of the reaction. No mathematical artifice or any unjustificed physicochemical assumption can replace the fundamental conceptual knowledge of the real process.