

# Closed algebraic expressions for the adiabatic limit value of the explosion constant in closed volume combustion

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## Abstract

An exact algebraic expression for the upper limit value of the explosion constant of gaseous fuels,  $K_{\max}$ , is derived by using a two-zone model for the adiabatic combustion in closed vessels. The expression is formulated in terms of the mean specific heat ratio of the unburned reactants  $\bar{\gamma}_u$  and introduces the concept of an apparent specific heat ratio of the burned products  $g_b$ . Computational data are presented for a set of representative fuels and for a range of equivalence ratio's, initial pressures and initial temperatures. A comparison of these data with correlations from literature shows that one correlation in particular is in close agreement with the exact result. This one-parameter correlation is based upon the almost linear relationship between the fraction of burned mass and the pressure, a relationship which is taken from the original work of Lewis and von Elbe. Based upon this theoretical work, formulas are suggested that can be used to estimate the explosion constant of fuel/air mixtures with a minimum level of computational effort. In addition, because the derivation in this paper is fairly straightforward and because the resulting expression is rather simple, the analysis presented in this paper can be used in combustion courses as an exercise in thermodynamics and as an illustration of the concept of the flame speed.

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## 1. Introduction

Combustible mixtures of air, and fuel gases or fuel vapors are often formed in industry, e.g. during the course of venting storage tanks or flaring of waste gases. The volumes that are involved in these operations are usually very large and the risk of accidental ignition, which can lead to destructive explosions is usually high. Safeguarding the infrastructure for excess damage in case of an accidental explosion involves, for instance, the placement of vents in the walls of the confinement. The key parameters for the design of such measures are the maximum pressure and the maximum rate of pressure rise that would occur if the mixture were to be ignited. The maximum rate of pressure rise depends upon the shape and size of the mixture confinement. Experiments in explosion vessels have

indicated that for most practical applications, the maximum rate of pressure rise follows a cubic-root law

$$\left. \frac{dP}{dt} \right|_{\max} V^{1/3} = \text{constant} = K \quad (1)$$

This observation has led to the definition of the parameter  $K$  which has been named explosion constant as well as deflagration index in the open literature. Two names are common:  $K_g$  is used for gases and  $K_{st}$  is used for dusts.

Models for predicting the maximum theoretical limit for  $K$ , i.e.  $K_{\max}$ , have been published in the literature. The maximum value is obtained for adiabatic combustion. Both Bradley and Mitcheson (1976) and Dahoe, Zevenbergen, Lemkowitz, and Scarlett (1996) present analytical expressions for the rate of pressure increase during combustion in a closed spherical vessel with central ignition. These expressions are both based upon a two-zone model which was previously developed by Lewis and von Elbe (1951). Dahoe et al. obtained a closed algebraic expression for  $K_{\max}$

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$$K_{\max} = (36\pi)^{1/3} (P_{\max} - P_0) \left( \frac{P_{\max}}{P_0} \right)^{1/\bar{\gamma}_u} S_f \quad (2)$$

where  $P_0$  and  $P_{\max}$  are, respectively, the initial and maximum pressure within the combustion vessel,  $S_f$  is the flame speed at maximum pressure and  $\bar{\gamma}_u$  is the average specific heat ratio of the unburned reactants. Cashdollar (2000) proposes a simpler expression which avoids the use of  $\bar{\gamma}_u$

$$K_{\max} = 4.84 (P_{\max} - P_0) \frac{P_{\max}}{P_0} S_f \quad (3)$$

where  $4.84 \approx (36\pi)^{1/3}$ . The model that is used to arrive at these two expressions is based upon assumptions that are somewhat restrictive in nature. The specific heats of reactants and products are assumed to remain constant and combustion is to take place within a spherical vessel. Moreover, these models do not contain the factor  $(\rho_u/\rho_b)$  which shows up in other models as an important parameter.

A survey of mainstream graduate textbooks on combustion, (e.g. Bartok & Sarofim, 1991; Borman & Ragland, 1998; Glassman, 1987; Kuo, 1986; Turns, 2000; Williams, 1985), shows that a discussion on  $K$  is absent in graduate level combustion teaching. On the other hand, discussions of a somewhat similar concept, the flame quenching distance, is usually presented. Both concepts can be used to illustrate the phenomena that are associated with travelling combustion waves. A reason why a discussion on  $K$  may not be included is that the two-zone model as it was introduced by Lewis and von Elbe is rather lengthy and misses somewhat the elegance of current two-zone models that have recently been presented within the scope of modelling internal combustion engines (Borman & Ragland, 1998).

Reference handbooks for engineers in the field, (e.g. Bartknecht, 1993), usually give tables of  $K$  for different fuels and for a variety of ranges of additional constraints and boundary conditions such as stoichiometry and initial pressure. However, they do not provide algebraic formulas to compute the explosion constant for a variety of conditions. Such formulas could be used, for example, to estimate the non-linear behavior of  $K$  with the mixing ratio of fuel mixtures or to quickly estimate the effect of stoichiometry, pressure and initial temperature.

## 2. Adiabatic two-zone model of closed volume combustion

Consider a closed volume  $V$  that at time  $t$  is split into two zones separated by a thin flame.  $V_u$  and  $M_u$  are the volume and mass of the zone in front of the flame that contains the unburned reactants. Likewise,  $V_b$  and  $M_b$  refer to the zone that contains the combustion products. This model has been called *thin-flame model* as well as *two-zone model* in the literature. Along with the assumption that the combustion

occurs in an infinitely thin flame, the other assumptions in this model are:

- Both the reactants and products behave as ideal gases.
- Adiabatic combustion.

These assumptions are less restrictive than those that are employed in the model by Dahoe et al. (1996)

Within a closed volume, the total mass, total volume and total internal energy are constant. These conditions can be expressed as follows

$$M_u + M_b = M \text{ or } \frac{dM_u}{dt} = -\frac{dM_b}{dt} \quad (4)$$

and

$$V_u + V_b = V \text{ or } \frac{dV_u}{dt} = -\frac{dV_b}{dt} \quad (5)$$

and

$$U_u + U_b = U \quad (6)$$

The mass exchange between the two zones is by definition of the flame speed  $S_f$ , given by:

$$\frac{dM_u}{dt} = -\rho_u A_f S_f \quad (7)$$

These equations can be used in combination with the assumption of ideal gas behavior to find an expression for the rate of increase of the combustion products volume  $V_b = M_b v_b$

$$\begin{aligned} \frac{dV_b}{dt} &= v_b \frac{dM_b}{dt} + M_b \frac{dv_b}{dt} \\ &= v_b \left( -\frac{dM_u}{dt} \right) + v_b \left( \frac{1}{v_b} \frac{dv_b}{dt} \right) \\ &= A_f v_b \rho_u S_f + v_b \left( \frac{1}{T_b} \frac{dT_b}{dt} - \frac{1}{P} \frac{dP}{dt} \right) \\ &= A_f v_b \rho_u S_f - \frac{V_b}{g_b} \left( \frac{1}{P} \frac{dP}{dt} \right) \end{aligned} \quad (8)$$

where  $g_b$  is related to the ratio of the relative change of products temperature to the relative change of pressure in a similar fashion as the specific heat ratio:

$$\left. \frac{P}{T_b} \frac{dT_b}{dP} \right|_{\text{twz}} = \frac{g_b - 1}{g_b} \quad (9)$$

$g_b$  is only marginally greater than 1. For instance, for the combustion of a stoichiometric methane/air mixture in a closed vessel,  $g_b$  changes from 1.1 at the start of the combustion to 1.06 at the end. Rearranging Eq. (8) yields the first rate equation for  $V_b$ :

$$\frac{1}{A_f} \frac{dV_b}{dt} = v_b \rho_u S_f - \frac{V_b}{g_b A_f} \left( \frac{1}{P} \frac{dP}{dt} \right) \quad (10)$$

A second rate equation for  $V_b$  can be derived from the energy equation for the unburned reactants. Under the assumption of adiabatic compression of the reactants zone, subject to mass exchange, the energy equation can be written as:

$$\frac{d(M_u u_u)}{dt} = -P \frac{dV_u}{dt} + h_u \frac{dM_u}{dt}$$

Expanding the term on the left and rearranging the equation yields:

$$\begin{aligned} M_u \frac{du_u}{dt} &= -P \frac{dV_u}{dt} + (h_u - u_u) \frac{dM_u}{dt} \\ &= -P \frac{d(M_u v_u)}{dt} + P v_u \frac{dM_u}{dt} = -P M_u \frac{dv_u}{dt} \end{aligned}$$

This last expression states that the unburned reactants are subject to an isentropic compression. Therefore:

$$\frac{dv_u}{dt} = -\frac{v_u}{\gamma_u P} \frac{dP}{dt}$$

This expression can be inserted into the rate expression for the reactants volume  $V_u$

$$\frac{dV_u}{dt} = v_u \frac{dM_u}{dt} + M_u \frac{dv_u}{dt} = -A_f S_f - \frac{V_u}{\gamma_u} \frac{1}{P} \frac{dP}{dt}$$

which then yields a second rate equation for the products volume:

$$\frac{1}{A_f} \frac{dV_b}{dt} = S_f + \frac{V_u}{\gamma_u A_f} \frac{1}{P} \frac{dP}{dt} \quad (11)$$

Eliminating the rate of volume increase from Eqs. (10) and (11) yields the evolution equation for the pressure:

$$\frac{1}{P} \frac{dP}{dt} = \frac{1}{V_u/\gamma_u + V_b/g_b} A_f (v_b \rho_u - 1) S_f \quad (12)$$

This equation has a rather simple interpretation which becomes evident by rewriting it as:

$$\frac{V_u}{\gamma_u P} \frac{dP}{dt} + \frac{V_b}{g_b P} \frac{dP}{dt} = A_f (v_b \rho_u - 1) S_f$$

The term on the right hand side represents the net rate of gas volume increase by combustion. This volume increase is absorbed by a pressure rise within the volume of unburned reactants (first term on the left hand side) and by a pressure rise within the volume of products (second term on the left hand side). The apparent similarity between  $\gamma_u$  and  $g_b$  is superficial. Whereas  $\gamma_u$  is a unique thermodynamic property of the reactants only,  $g_b$  is a thermodynamic property of the reactants/products mixture and has meaning only within the scope of the two-zone model. The parameter  $g_b$  is defined by Eq. (9) and varies during the progression of the combustion. According to Bradley and Mitcheson (1976), several researchers assumed that this parameter is equal to the specific heat ratio of the products,  $\gamma_{b, \text{frozen}}$ , if as the temperature rise of the products zone were the mere result of an adiabatic compression at frozen equilibrium.

However, for stoichiometric mixtures of hydrocarbon fuels,  $\gamma_{b, \text{frozen}}$  is of the order of 1.25 which is much greater than  $g_b$ . Numerical computations have revealed that  $g_b$  is still substantially smaller than  $\gamma_{b, \text{shift}}$  with the latter parameter defined for a mixture subject to shifting chemical equilibrium. For stoichiometric mixtures of hydrocarbon fuels,  $\gamma_{b, \text{shift}}$  is of the order of 1.17. The existence of the two zones with a compressible reaction zone and a compressible products zone, subject to a shifting equilibrium, provides an extra degree of freedom for the chemical equilibrium to settle in the explosion vessel. According to Le Chatelier's principle, this global equilibrium will settle in order to maximally resist the change of state brought by the progression of the combustion. It turns out that the combustion products are more elastic in a two-zone environment than in a mono-zone environment.  $g_b$  is a unique thermodynamic property of the fuel/air/products mixture within the context of the two-zone model and cannot be computed by a model different from the defining two-zone model itself.

Within the limitations set by the assumption of adiabatic combustion and the two-zone model, Eq. (12) is exact. This equation should be compared to the expression that was derived for central ignition in a spherical vessel by Bradley and Mitcheson (1976) and later by Dahoe et al. (1996):

$$\frac{dP}{dt} = \frac{3(P_{\max} - P_0)}{R_{\text{vessel}}} \left[ 1 - \left( \frac{P_0}{P} \right)^{1/\gamma_u} \frac{P_{\max} - P}{P_{\max} - P_0} \right]^{2/3} \left( \frac{P}{P_0} \right)^{1/\gamma_u} S_f \quad (13)$$

This latter expression is seemingly more practical because the right hand side contains only the pressure. However, it is significantly different from the exact rate equation, Eq. (12), because this latter equation suggests that the rate of pressure increase is proportional to the pressure itself, whereas Eq. (13) suggests a different dependence. The reason for this difference is that to arrive at this latter expression, one must additionally assume that:

$$\frac{M_b}{M_u + M_b} = \frac{P - P_0}{P_{\max} - P_0} \quad (14)$$

This remarkable equation, originally derived by Lewis and von Elbe (1951) is in fact only an approximation and use of it leads to small errors which, as will be shown, can be corrected for in a simple manner.

Adiabatic combustion results in a maximum pressure at the end of combustion. Because the rate of pressure increase is proportional to pressure, the explosion constant is maximal at the end of combustion where  $V_b \rightarrow V$ ,  $V_u \rightarrow 0$  and  $P \rightarrow P_{\max}$ . Using the definition equation for  $K$  and the rate equation, Eq. (12) yields

$$K_{\max} = \frac{O_f}{V^{2/3}} g_b (v_b \rho_u - 1) P_{\max} S_f \quad (15)$$

$O_f$  is the final flame area just before the flame is extinguished. For central ignition of premixed gases in

closed spherical vessels, the ratio  $O_f/V^{2/3}$  is  $(36\pi)^{1/3} = 4.836$ . The formula above can be further written in other terms. The densities can be written as

$$v_b = \frac{1}{\rho_b} = \frac{V}{M} = \frac{1}{\rho_{u0}} \text{ and } \rho_u = \rho_{u0} \left( \frac{P_{\max}}{P_0} \right)^{1/\bar{\gamma}_u}$$

where  $\bar{\gamma}_u$  is the mean heat capacity ratio of the reactants along the path of isentropic compression from the start of combustion to the end. With these relationships, the  $K$ -expression for spherical vessels finally results in a two parameter equation

$$K_{\max} = 4.836 g_b \left[ \left( \frac{P_{\max}}{P_0} \right)^{1/\bar{\gamma}_u} - 1 \right] P_{\max} S_f \quad (16)$$

with  $\bar{\gamma}_u$  and  $g_b$  as parameters.  $S_f$  is the flame speed at the final phase of the combustion and can be estimated from graphs or tables published in the literature, (e.g. Borman & Ragland, 1998).  $P_{\max}$  is the pressure of the theoretical final state which is the state that is in chemical equilibrium with the initial state, constrained by constant volume and constant internal energy. For a given fuel/air mixture, equivalence ratio, initial temperature and initial pressure,  $P_{\max}$  can be computed with a chemical equilibrium program.

### 3. Results and discussion

A numerical solution of the adiabatic two-zone model with a constant flame speed has been performed using software provided by the CHEMKIN II library (Kee, Rupley, & Miller, 1994). The accompanying thermodynamic database is the one that is made available online by Burcat (2003). The model uses the VODE-solver (Brown, Byrne, & Hindmarch, 1989) to numerically integrate the combustion-rate equation, Eq. (7), while continuously conserving mass, Eq. (4), volume, Eq. (5), and internal energy, Eq. (6), to solve for the pressure and temperatures of the reactants and products. Within the VODE-solver, the implicit Adams method with functional iteration (no Jacobian) is selected (method flag=10) in combination with a variable time step (itask parameter=1) and a relative error tolerance of  $5 \times 10^{-8}$ . To compute the progress of the volume of burned products, the initial value of this volume must be set to a non-zero value. Numerical exercises proved that the computed  $K$  factor is independent of this initial value.

The parameters  $\bar{\gamma}_u$  and  $g_b$  have been computed for mixtures of air with methane, propane, hydrogen, acetylene and methanol, and the results are shown in Figs. 1 and 2 with the equivalence ratio as independent variable. The initial temperature and pressure are respectively 298.15 K and 1 atm. The results indicate that the parameter  $\bar{\gamma}_u$  varies substantially with the fuel and the mixing ratio. To obtain a 2% accuracy on  $K_{\max}$ ,  $\bar{\gamma}_u$  needs to be estimated within an accuracy better than 1.10%. From Fig. 1, it can be judged

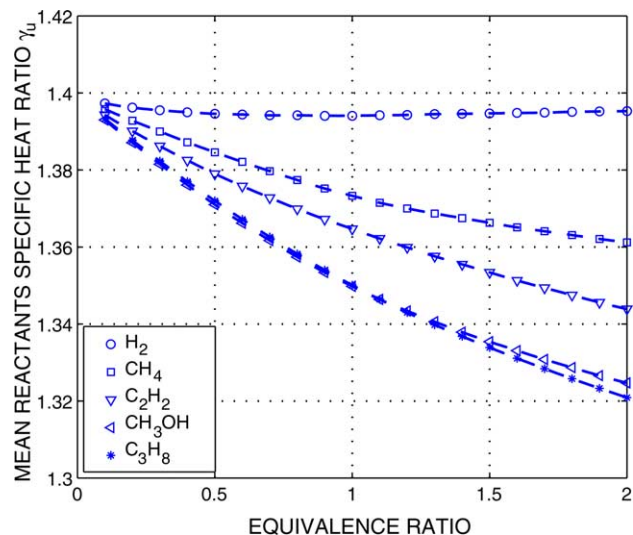


Fig. 1. Mean reactants specific heat ratio  $\bar{\gamma}_u$  for selected fuel/air mixtures at 25 °C and 1 atm.

that this is a rather challenging task if one does not have access to all the necessary computer programs. On the other hand, the parameter  $g_b$  can be estimated from Fig. 2 with an accuracy of about 2%. Because  $K_{\max}$  is linear in  $g_b$ , this is also the resulting uncertainty on  $K_{\max}$ .

Fig. 3 shows the ratio of  $K_{\max}/S_f$  for the different fuels as a function of the stoichiometric ratio. The explosion constant reaches a maximum for slightly rich mixtures because these mixtures also show the highest combustion temperature. Only for acetylene does  $K_{\max}/S_f$  continue to increase. Methanol and propane show an almost identical behavior.

The initial pressure has a negligible effect on both  $\bar{\gamma}_u$  and  $g_b$ . For a five-fold increase in pressure,  $\bar{\gamma}_u$  does not decrease more than 0.01% and  $g_b$  does not increase more than 0.4%. Whereas this effect can readily be understood for

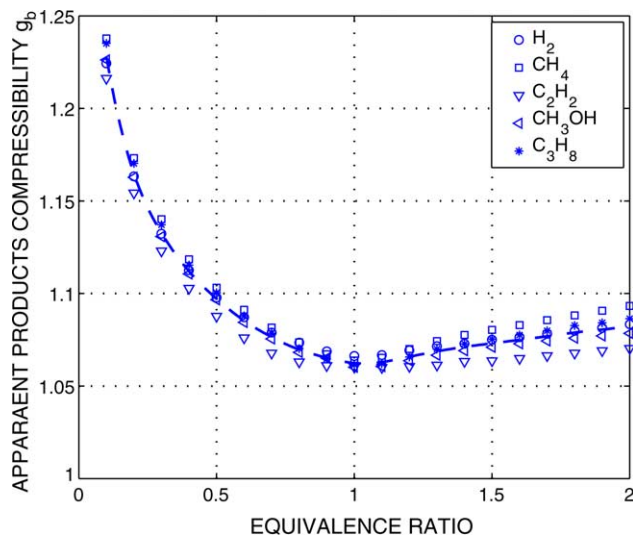


Fig. 2. Apparent products specific heat ratio  $g_b$  for selected fuel/air mixtures at 25 °C and 1 atm.

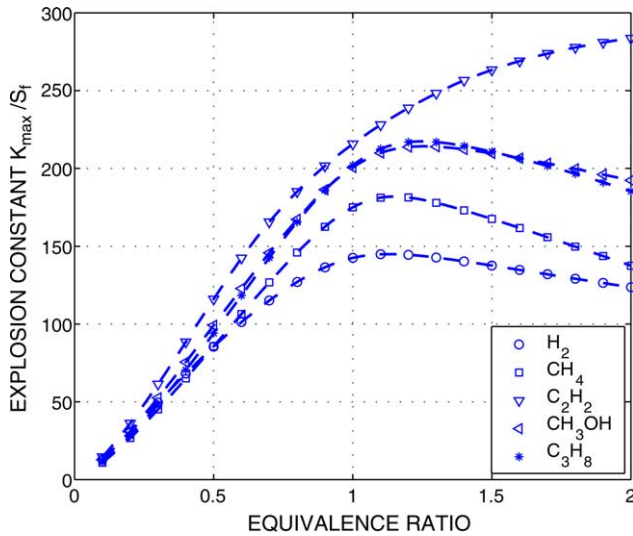


Fig. 3. The relative explosion constant  $K_{\max}/S_f$  of selected fuel/air mixtures at 25 °C and 1 atm.

the unburned reactants, the minor increase of  $g_b$  can be explained as follows.

The adiabatic flame temperature of hydrocarbon combustion increases with pressure because the increase of pressure disfavors the dissociation of heavy combustion products such as  $\text{CO}_2$  and  $\text{H}_2\text{O}$  into lighter products. As a consequence, the specific heats of the product mixture decrease and the specific heat ratio increases. However, this effect is only important in the pressure range of 1 to 10 atm. With closed volume combustion, high pressures outside this range are readily obtained and this explains the small effect on  $g_b$ .

The initial temperature of the reactants mixture has a strong effect on  $\tilde{\gamma}_u$  and a slight effect on  $g_b$ . Increasing the initial temperature increases the end-of-combustion temperature to a lesser extent and reduces the maximum pressure almost inversely because of the likewise reduction in initial mass.  $g_b$  increases almost linear to the initial temperature with  $d(g_b)/dT \approx 5 \times 10^{-5}$ . The reason for this minor increase is the stronger reduction in  $\tilde{\gamma}_u$  which increases the elasticity of the reactants volume. As a consequence, the products volume is less strained.

Eq. (15) shows that  $K$  is proportional to the flame speed and the maximum pressure. The proportionality coefficient in this equation includes the term  $(v_b \rho_u - 1)$ . Bradley and Mitcheson (1978) found the parameter  $(v_b \rho_u - 1)S_f$  to be the single most important mixture parameter in the theory of venting during explosions.

The two-parameter formula, Eq. (16), can be compared to the other theoretical formulas that have been presented in the literature. The one-parameter expression derived by Dahoe et al. (1996) is given by Eq. (2) whereas the zero-parameter expression by Cashdollar (2000) is given by Eq. (3). Fig. 4 shows the comparison of these expressions in comparison to the exact numerical solution. Whereas the formula proposed by Cashdollar overestimates  $K_{\max}$  with

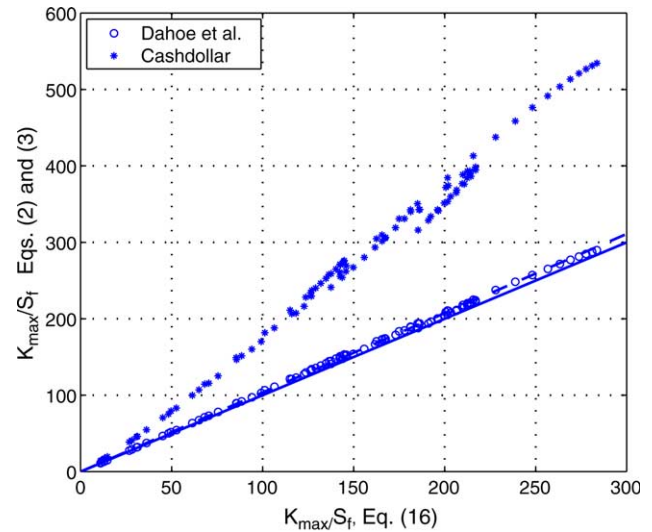


Fig. 4. Comparison of different correlations with the exact theoretical solution, different fuels.

about 50%, the expression by Dahoe et al. systematically overestimates  $K_{\max}$  with about 4%. The reason for this systematic overestimation is that the Lewis and von Elbe relationship, Eq. (14), systematically underestimates the pressure for a given mass fraction. In order to understand this systematic, it is necessary to revisit the Lewis and von Elbe relationship.

#### 4. The Lewis and von Elbe relationship revisited

Lewis and von Elbe (1951) studied the evolution of the pressure in a closed volume combustion process and found that

$$\frac{P - P_0}{P_{\max} - P_0} \approx n \quad (17)$$

where  $n$  is the molar fraction of burned products. The original derivation of this relationship is omitted in all the major text books on combustion and in all of the most relevant publications. However, by using the two zone model the derivation becomes rather straightforward. Under the assumption that the number of moles of burned gas per mole of unburned gas remains constant during the combustion process, it can be shown that

$$\begin{aligned} N_u &= N_i(1 - n) \\ N_b &= N_e n \end{aligned} \quad (18)$$

where  $N_i$  is the initial number of moles of unburned reagents and  $N_e$  is the final number of moles of burned products.  $N_u$  and  $N_b$  are, respectively, the actual number of moles of unburned and burned gases. The pressure can be linked to the number of moles using the ideal gas law. Applied to the volumes of the two zones individually and to the total volume, one arrives at

$$\begin{aligned}
 PV_u &= RN_u T_u & P_i V &= RN_i T_i \\
 PV_b &= RN_b T_b & P_e V &= RN_e T_e \\
 PV &= R(N_u T_u + N_b T_b)
 \end{aligned} \tag{19}$$

where the indices *i* and *e* refer to the initial and final condition, respectively. Using the concept of *n*, one can rewrite this last expression as:

$$\begin{aligned}
 \frac{PV}{R} &= N_u T_u + N_n T_b = N_i(1-n)T_u + N_e n T_b \\
 &= N_i T_u + n(N_e T_b - N_i T_u)
 \end{aligned} \tag{20}$$

$$\begin{aligned}
 \frac{T_u - T_i}{T_i} &= \left(\frac{P}{P_i}\right)^{(\gamma_u-1)/\gamma_u} - 1 \approx \left(\frac{1}{2} + \frac{1}{2} \frac{P_{\max}}{P_0}\right)^{(\gamma_u-1)/\gamma_u} - 1 \approx \frac{\gamma_u - 1}{\gamma_u} \sqrt{2} \ln\left(\frac{1}{2} \frac{P_{\max}}{P_0}\right) \\
 \frac{T_e - T_b}{T_e} &= 1 - \left(\frac{P}{P_e}\right)^{(g_b-1)/g_b} \approx 1 - \left(\frac{1}{2} + \frac{1}{2} \frac{P_0}{P_{\max}}\right)^{(g_b-1)/g_b} \approx \frac{g_b - 1}{g_b} \frac{\ln(2)}{\sqrt{2}}
 \end{aligned} \tag{22}$$

Using the expressions for  $P_i = P_0$  and  $P_e = P_{\max}$ , one arrives at:

$$\begin{aligned}
 \frac{P - P_0}{P_{\max} - P_0} &= \frac{N_i(T_u - T_i) + n(N_e T_b - N_i T_u)}{N_e T_e - N_i T_i} \\
 &= n + \frac{(1-n)N_i(T_u - T_i) - nN_e(T_e - T_b)}{N_e T_e - N_i T_i} \approx n
 \end{aligned} \tag{21}$$

Bradley and Mitcheson (1976) were the first to use the Lewis and von Elbe relationship in its approximative form in their analysis. However, they took *n* to be the mass fraction of burned products instead of the molar fraction. Dahoe et al. (1996) made the same approximation. Fig. 5 shows the molar and mass deficits from the Lewis and von

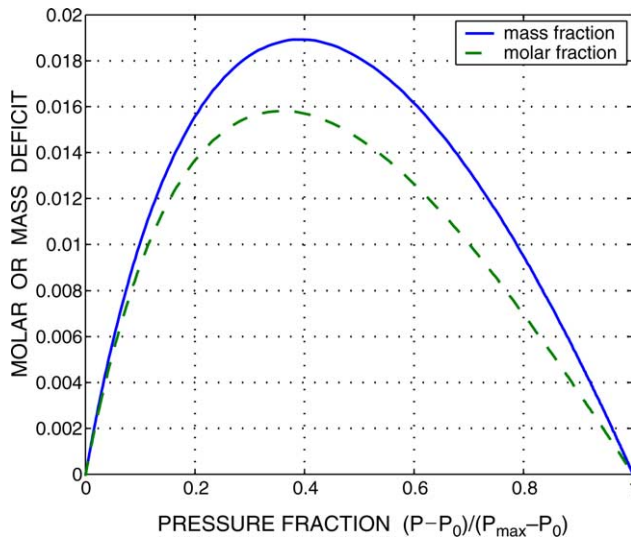


Fig. 5. Molar or mass deficit (see text for definitions) for a stoichiometric methane/air mixture at 20 °C and 1 atm. initially.

Elbe relationship during the combustion of a methane/air mixture. The molar deficit is defined as  $(P - P_0)/(P_{\max} - P_0) - N_b/(N_u + N_b)$  whereas the mass deficit is  $(P - P_0)/(P_{\max} - P_0) - M_b/(M_u + M_b)$ . Because the mass deficit is larger than the molar deficit, the error in using the approximative form for the mass fraction is somewhat larger.

The nominator of the second term on the right hand side of Eq. (21) is a difference of two terms that are both zero for  $n=0$  and  $n=1$ . As shown in Fig. 5, the nominator reaches a maximum for  $n \approx 1/2$ . An error analysis of the corrective term can be made using first order approximations for  $n = 1/2$  with  $P \approx 0.5P_{\max} + 0.5P_0$  and  $P_{\max} \geq 5P_0$ :

In addition, the following relationship holds:

$$\frac{N_e T_e}{N_i T_i} = \frac{P_{\max}}{P_0} \tag{23}$$

A further analysis along this line shows that the second term on the right hand side of Eq. (21) is of secondary order when compared to *n* and shows also that the correction term increases monotonically with  $P_{\max}/P_0$ . The correction is larger at higher explosion loads. This explains the systematic error of the Dahoe equation for *K*, Eq. (2).

The error in predicting the pressure evolution when using the approximative form of the Lewis and von Elbe relationship is somewhat larger than the numbers in Fig. 5 would suggest, because the rate analysis involves the derivatives. As the combustion proceeds towards the end, the pressure strives towards its final equilibrium value and the rate of pressure increase at the end of the combustion is predicted too high by models that rely on the approximative equation. On the other hand, these models predict a too low rate of pressure increase in the beginning phase of the explosion. Interestingly, Dahoe and de Goeij (2003) used a two-zone model to extract laminar flame speeds from closed volume combustion experiments with the Dahoe bomb, as described by Eckhoff (2003). They fitted the model to experimental pressure–time curves in the initial stage of the explosions. The derived flame speeds are found to be systematically too high when compared to other experimental values. Dahoe and de Goeij report a systematic error of about 5% for low flame speeds to 10% for high flame speeds. This discrepancy is consistent with the manner in which the Lewis and von Elbe relationship underestimates the pressure. It may be verified that at low flame speeds, for example, about 4% out of the 5% error may be attributed to the use of the approximative form of the relationship.

## 5. Further discussion and recommended correlation

In order to predict the adiabatic limit value for  $K$  for a given fuel/air mixture and initial conditions, the correct equation, Eq. (16), could be used. However, this correlation employs the two mixture parameters  $g_b$  and  $\tilde{\gamma}_u$ , next to  $S_f$  and  $P_{\max}$ . These former parameters may be hard to estimate without the necessary computer programs. To develop a useful correlation for predicting the  $K$  value, computer simulations of adiabatic closed volume combustion have been carried out for five fuels:  $\text{CH}_4$ ,  $\text{C}_3\text{H}_8$ ,  $\text{H}_2$ ,  $\text{C}_2\text{H}_2$  and  $\text{CH}_3\text{OH}$ . Twenty equally spaced values between 0.1 and 2.0 are used for the equivalence ratio, five equally spaced values between 1 and 5 are used for the initial pressure and five equally spaced values between 100 and 500 °C are used for the initial temperature. The computed  $K$  values are used to develop empirical correlations that are derived from the theoretical correlations.

A zero parameter correlation, i.e. the Cashdollar expression, can be tuned to a better fit by adjusting the proportionality coefficient:

$$K_{\max} = \frac{4.836}{1.492} (P_{\max} - P_0) \frac{P_{\max}}{P_0} S_f$$

This correlation fits the theoretical results with a relative error with a mean value of zero and a standard deviation of 10.2%.

The Dahoe equation for  $K$ , containing one parameter, was fitted with a least-squares procedure to the computed data to give

$$K_{\max} = \frac{4.836}{1.041} (P_{\max} - P_0) \left( \frac{P_{\max}}{P_0} \right)^{1/\tilde{\gamma}_u} S_f$$

in which  $\tilde{\gamma}_u$  is computed exactly by the computer program. This correlation fits the theoretical results for these five fuels with a mean error of zero and a standard deviation of only 1.29%. This equation still needs one parameter,  $\tilde{\gamma}_u$ , which may be hard to estimate. However, a mean value of  $\tilde{\gamma}_u$  of 1.33 may be used to yield

$$K_{\max} = \frac{4.836}{1.040} (P_{\max} - P_0) \left( \frac{P_{\max}}{P_0} \right)^{1/1.33} S_f \quad (24)$$

which gives a relative error with a mean value of zero and a standard deviation of 4.5%.

Finally, the correct equation, Eq. (16), could also be simplified by using the mean values for  $g_b = 1/0.900$  and  $\tilde{\gamma}_u = 1.330$  which gives

$$K_{\max} = \frac{4.836}{0.900} \left[ \left( \frac{P_{\max}}{P_0} \right)^{1/1.33} - 1 \right] P_{\max} S_f \quad (25)$$

This equation fits the theoretical results with a mean relative error of zero and a standard deviation of 5.4%. This error is somewhat larger than the zero-parameter version of the Dahoe expression. However, this

correlation does capture the underlying physics somewhat better because of the presence of the  $(\rho_u/\rho_b - 1)$  term as explained earlier.

The two zero-parameter equations, Eqs. (24) and (25), can be recommended for practical use. For a given fuel/air mixture, equivalence ratio, initial temperature and initial pressure,  $P_{\max}$  can be computed with a chemical equilibrium program, such as the CEA program made available online by NASA (McBride, 2004).

## 6. Conclusion

A review and an analysis of expressions for the theoretical adiabatic limit value for the explosion constant  $K$  of fuel/air mixtures is presented. An exact expression has been derived that employs two fluid properties: the ratio of the specific heat of the unburned reactants and an apparent specific heat ratio of the burned products. Theoretical  $K$ -values have been computed for a set of representative fuels and are fitted to the theoretical expressions. As a result, two zero-parameter expressions are presented that fit the theoretical data with an accuracy of 5%. These closed correlations are fairly simple to use and can be used to rapidly estimate the explosion constant of a fuel/air mixture. In addition, the analysis presented in this paper is of intermediate graduate level and can be used in combustion courses to illustrate the phenomena of traveling combustion waves.

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