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PRESSURE RISE IN CONFINED GAS EXPLOSIONS

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Summary

Simple methods to model pressure rise in confined gas explosions are reviewed. The simplest method is based on energy conservation in an adiabatic system. Algebraic equations by which pressure and flame front radius as functions of time can be calculated have been derived by making the so-called isothermal approximation. This approximation assumes constant temperatures for the unburned and burned gases and neglects the pressure dependence of the burning velocity. At early times the overpressure is proportional to t^3.

Expansion factors and AICC pressure ratios were calculated for hydrogen mixed with dry or humid air at different concentrations. Only the dissociation of water vapour to hydrogen and oxygen was modelled. The values of AICC pressure ratio at 100 % relative humidity calculated with this method were found to be within 2.8 % of the values given in literature.

Four methods to calculate pressure rise were used to calculate the amount of hydrogen whose combustion generates a 2 kPa overpressure in a $1000\ m^3$ enclosure. The simple method based on energy conservation was taken as reference. The method based on isothermal approximation gave results that were close to those calculated by the simple method.

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1 INTRODUCTION

The maximum overpressure of a confined gas explosion is quite easily calculated. The time dependence of the overpressure, however, is more difficult to model. The pressure rises fast to its maximum value as a flame front propagates in the enclosure, converting cold gas mixture to hot combustion products. Pressure decay is a slower effect due to loss of heat from combustion products to the walls of the enclosure.

The main reason to model pressure rise in confined explosions has been the need to calculate the flame speed of a mixture from measured pressure values. The models can also be used to calculate the minimum amount of burned gas required to open explosion relief panels in a vented explosion. The purpose of the present study is to evaluate the suitability of different models of confined explosion presented in open literature for this problem.

2 SIMPLE EXPLOSION MODELLING

2.1 MAXIMUM PRESSURE

The basis for all simple models is conservation of energy E [J] for an adiabatic, constant volume system. This provides a unique relationship between the average pressure P [Pa] and the amount of burned gas m_b [kg]. For an ideal gas with a constant ratio of specific heats $C_p/C_v = \gamma$ and specific heat of combustion h_c [J/kg], this relationship is (Shepherd et al. 1997)

$$E = \frac{PV}{\gamma - 1} - h_c m_b \qquad (1)$$

where V [m^3] is the volume of the enclosure. Initially, $m_b = 0$ and $P = P_0$ [Pa]. Subtracting the values of Eq. (1) at these times from each other, one finds

$$\Delta P = P - P_0 = (\gamma - 1)\frac{h_c m_b}{V} \qquad (2)$$

The maximum pressure P_m [Pa] is obtained when all of the gas is burned: $m_b = m_0$ where m_0 [kg] is the total mass of the gas. The ratio P_m/P_0 is called AICC (Adiabatic Isochoric Complete Combustion) pressure ratio.

2.2 EXPLOSION DEVELOPMENT

Differentiation of Eq. (1) with respect to time gives (Shepherd et al. 1997)

$$\frac{V}{\gamma - 1}\frac{dP}{dt} = h_c \frac{dm_b}{dt} \tag{3}$$

Solving for the ratio of $V/(\gamma-1)$ in Eq. (2) and inserting in Eq. (3) gives

$$\frac{dP}{dt} = \frac{\Delta P_m}{m_0}\frac{dm_b}{dt} \tag{4}$$

where ΔP_m is the maximum overpressure: $\Delta P_m = P_m - P_0$.

The rate at which gas is being burned can be computed by considering the flame as having an area $A_f(t)$ and consuming unburned gas of density ρ_u [kg/m^3] with a laminar burning velocity S_u [m/s]

$$\frac{dm_b}{dt} = A_f \rho_u S_u \tag{5}$$

Since the volume occupied by the combustion products is larger than the volume of the unburned gas mixture, the flame propagation always results in displacement of the surrounding gas. Therefore the apparent laminar flame speed is higher than the laminar burning velocity up to a factor of ρ_u/ρ_b, where ρ_b [kg/m^3] is the density of the burned gas.

The effect of turbulence is to distort the flame front and increase the product $A_f S_u$ substantially. Engineering models usually treat turbulent flame propagation by replacing the burning velocity S_u with an effective "turbulent" value S_T [m/s] and interpreting the area A_f as the area of a smooth surface passing through the average location of the turbulent flame.

As the flame propagates through the enclosure, the pressure P increases uniformly in space, compressing both unburned and burned gases. This is a good approximation because the flame speed is small relative to the sound velocity.

If the effects of heat transfer during the burn can be neglected, the unburned gases are spatially uniform and conditions can be predicted by using the isentropic relationships

$$T_u = T_0 \left(\frac{P}{P_0}\right)^{\frac{\gamma-1}{\gamma}} \tag{6}$$

$$\rho_u = \rho_0 \left(\frac{P}{P_0}\right)^{\frac{1}{\gamma}} \tag{7}$$

For a given fuel concentration, the burning velocity S_u is dependent on both temperature and pressure. For the purpose of engineering studies, the dependence is usually taken to be

$$S_u = S_0 \left(\frac{P_0}{P} \right)^{\beta} \left(\frac{T_u}{T_0} \right)^2 \tag{8}$$

The exponent β is substance specific. Actually, the pressure dependence of S_u is quite weak since the value of β is about -0.25 for hydrocarbons (Shepherd et al. 1997) and about -0.2 for lean hydrogen-air mixtures (Gelfand 2000).

Nagy et al. (1969) have derived differential equations for P and r_b assuming a spherical flame front and equal specific heat ratios γ of the unburned and burned gases, respectively. (They note that it is possible to derive equations with different specific heat ratios, but these become unwieldy.) The temperature of burned gas T_b is assumed to vary adiabatically with pressure P

$$T_b = T_m \left(\frac{P_m}{P} \right)^{\frac{1}{\gamma}-1} \tag{9}$$

This, however, is a questionable assumption in a model of the initial phase of the explosion when the pressure P is low. It leads to a considerable underestimation of T_b in this phase. Assume, for example, a stoichiometric hydrogen-air mixture with $P_m/P_0 = 8$, $T_m = 2700$ K and $\gamma = 1.4$. Eq. (9) gives an initial value of the burned gas temperature of 1490 K. This is almost 1000 K lower than the adiabatic flame temperature of the mixture! However, when the entire course of a confined explosion is modelled, the adiabatic approximation is reasonable (Nagy et al. 1971).

The original equations by Nagy et al. (1969) have been simplified by Bradley and Mitcheson (1976). The differential equation for the pressure P is

$$\frac{dP}{dt} = \frac{3\gamma S_u P}{R_e} \left(\frac{P_m^{2/3}}{P_0} \right)^{1/\gamma} \left(P_m^{1/\gamma} - P_0^{1/\gamma} \right)^{1/3} \left[1 - \left(\frac{P_0}{P} \right)^{1/\gamma} \right]^{2/3} \tag{10}$$

where R_e [m] is the radius of a sphere with a volume equal to V

$$R_e = \left(\frac{3V}{4\pi} \right)^{1/3} \tag{11}$$

The pressure dependence of the burning velocity S_u in Eq. (10) is found by inserting Eq. (6) into Eq. (8)

$$S_u = S_0 \left(\frac{P}{P_0} \right)^{2 - \frac{2}{\gamma} - \beta} \tag{12}$$

The differential equation for the radius of the flame front r_b [m] is

$$\frac{dr_b}{dt} = S_0 \left(\frac{P_m}{P_0} \right)^{1/\gamma} \left\{ 1 - \left[1 - \left(\frac{P_0}{P_m} \right)^{1/\gamma} \right] \left(\frac{r_b}{R_e} \right)^3 \right\}^{3 - 2\gamma + \beta\gamma} \tag{13}$$

and the relation between P and r_b

$$\left(\frac{r_b}{R_e} \right)^3 = \frac{1 - \left(\frac{P_0}{P} \right)^{1/\gamma}}{1 - \left(\frac{P_0}{P_m} \right)^{1/\gamma}} \tag{14}$$

The system of equations (10), (13) and (14) can only be solved numerically. Nagy et al. (1969) simplify these equations by making the so-called isothermal approximation. In this approximation the temperatures of the unburned and burned gases are constant. The corresponding equations can be derived by setting $\gamma = 1$ in Eqs. (10), (13) and (14). The differential equation for P becomes

$$\frac{dP}{dt} = \frac{3S_u}{R_e} P_m^{2/3} \frac{P}{P_0} \left(P_m - P_0 \right)^{1/3} \left(1 - \frac{P_0}{P} \right)^{2/3} \tag{15}$$

The differential equation for r_b is simplified to

$$\frac{dr_b}{dt} = S_u \frac{P_m}{P_0} \left[1 - \left(1 - \frac{P_0}{P_m} \right) \left(\frac{r_b}{R_e} \right)^3 \right]^{1+\beta} \tag{16}$$

and the relation between P and r_b to

$$\left(\frac{r_b}{R_e} \right)^3 = \frac{1 - \frac{P_0}{P}}{1 - \frac{P_0}{P_m}} \tag{17}$$

The system of equations (15) to (17) of the isothermal approximation can be solved only numerically. Nagy et al. (1971) have integrated Eq. (15) numerically and found that the resulting pressure vs. time curve coincides with the experimental data points of a 9.4 % methane-air mixture in a cubical 28-dm^3 vessel up to about one third of the maximum pressure. At later times, the measured pressure was less than predicted by Eq. (14) because the flame front was no longer spherical.

The adiabatic approximation Eq. (10) was found to give a better prediction of the dependence of the burning velocity of initially quiescent methane-air mixture on methane concentration than the isothermal approximation Eq. (14). Test results of dust explosions in closed vessels could not be used with Eq. (10) or Eq. (14) to derive the turbulent burning velocity S_T of dust-air mixtures since the latter varied with the type and concentration of dust. Eq. (14) with approximate values of several of the constants was used to derive the burning velocity of dust mixtures from the maximum pressure and the maximum rate of pressure rise measured in the Hartmann tube (Nagy et al. 1971).

If the exponent β in Eq. (8) is set equal to zero, the differential equations (15) and (16) can be solved by separation of variables, giving a set of three algebraic equations for P, r_b and t. Note that the insertion of $\gamma = 1$ and $\beta = 0$ into Eq. (12) gives $S_u = S_0$.

The equation (15) can be written as

$$\frac{dP}{dt} = 3k\left(P - P_0\right)^{2/3} P^{1/3} \tag{18}$$

where the constant k is defined as

$$k = \frac{S_0 P_m^{2/3}}{R_e P_0}\left(P_m - P_0\right)^{1/3} = \frac{S_0 P_m}{R_e P_0}\left(1 - \frac{P_0}{P_m}\right)^{1/3} \tag{19}$$

By separating the variables in Eq. (18) and integrating from P = P_0 at t = 0 to P = P at t = t one finds

$$\int_{P_0}^{P} \frac{dP}{(P - P_0)^{2/3} P^{1/3}} = 3kt \tag{20}$$

The integral in Eq. (20) can be reduced to a standard one by substitution

$$x = \left(1 - \frac{P_0}{P}\right)^{1/3} \tag{21}$$

The resulting definite integral is

$$\int_{0}^{(1-P_0/P)^{1/3}} \frac{dx}{1 - x^3} = kt \tag{22}$$

The tabulated indefinite integral is (Spiegel 1968)

$$\int \frac{dx}{x^3 - a^3} = \frac{1}{6a^2} \ln \frac{(x-a)^2}{x^2 + ax + a^2} - \frac{1}{a^2\sqrt{3}} \arctan \frac{2x+a}{a\sqrt{3}} \tag{23}$$

The algebraic equation for the pressure P becomes

$$-\frac{1}{6} \ln \frac{\left[(1-P_0/P)^{1/3} - 1\right]^2}{(1-P_0/P)^{2/3} + (1-P_0/P)^{1/3} + 1} + \frac{1}{\sqrt{3}} \arctan \frac{2(1-P_0/P)^{1/3} + 1}{\sqrt{3}}$$

$$-\frac{1}{\sqrt{3}} \arctan \frac{1}{\sqrt{3}} = kt \tag{24}$$

Eq. (16) with β = 0 can be integrated from r = 0 at t = 0 to r = r_b at t = t

$$\int_0^{r_b} \frac{dr}{1-(1-P_0/P_m)(r/R_e)^3} = S_0 \frac{P_m}{P_0} t \tag{25}$$

The integral (25) can be reduced to the tabulated one Eq. (23) by the substitution x = r/R_e.

$$\int_0^{r_b/R_e} \frac{R_e dx}{1-(1-P_0/P_m)x^3} = -\frac{R_e}{1-P_0/P_m} \int_0^{r_b/R_e} \frac{dx}{x^3 - a^3} = S_0 \frac{P_m}{P_0} t \tag{26}$$

where the constant a is now

$$a = \frac{1}{(1-P_0/P_m)^{1/3}} \tag{27}$$

By using the definition of the constant k, Eq. (19), the equation (26) is simply

$$-\int_0^{r_r/R_e} \frac{dx}{x^3 - a^3} = kt \tag{28}$$

The resulting algebraic equation for r_b is

$$-\frac{1}{6} \ln \frac{\left(\frac{r_b}{R_e} - \frac{1}{(1-P_0/P_m)^{1/3}}\right)^2}{\left(\frac{r_b}{R_e}\right)^2 + \frac{r_b/R_e}{(1-P_0/P_m)^{1/3}} + \frac{1}{(1-P_0/P_m)^{2/3}}} + \frac{1}{\sqrt{3}} \arctan \frac{1}{\sqrt{3}} \left[\frac{2r_b}{R_e}\left(1 - \frac{P_0}{P_m}\right)^{1/3} - 1\right]$$

$$-\frac{1}{\sqrt{3}} \arctan \frac{1}{\sqrt{3}} = kt \tag{29}$$

Of course, the algebraic equations (24) and (29) cannot be solved to give expressions for pressure P and radius r_b as functions of time t. However, the values of P and r_b at a given time t can be found by iteration of these equations.

2.3 THE CUBE LAW

It is known from experiments that the overpressure ΔP at early times is proportional to the cube of time. One form of the cube law can be derived by expanding the integrand in Eq. (20) as a power series (Nagy et al. 1969). Change the variable P to $z = P/P_0 - 1$.

$$\int_0^{P/P_0-1} \frac{dz}{z^{2/3}(1+z)^{1/3}} = \int_0^{P/P_0-1} \left(z^{-2/3} - \frac{1}{3} z^{1/3} + \frac{2}{9} z^{4/3} - \ldots \right) dz = 3kt \tag{30}$$

The series expansion is valid for $-1 < z \le 1$ or $0 < P \le 2P_0$. The result is

$$3\left(\frac{P-P_0}{P_0}\right)^{1/3} - \frac{1}{4}\left(\frac{P-P_0}{P_0}\right)^{4/3} + \frac{2}{21}\left(\frac{P-P_0}{P_0}\right)^{7/3} - \ldots = 3kt \tag{31}$$

For small overpressures ($P - P_0 << P_0$) only the first term in the series is significant

$$\left(P-P_0\right)^{1/3} \approx P_0^{1/3} kt = \frac{S_0}{R_e}\left(\frac{P_m}{P_0}\right)^{2/3}\left(P_m - P_0\right)^{1/3} t \tag{32}$$

Raising both sides of Eq. (32) to the third power gives the cube law

$$\Delta P = P - P_0 = \left(P_m - P_0\right)\left(\frac{P_m}{P_0}\right)^2 \left(\frac{S_0 t}{R_e}\right)^3 \tag{33}$$

Of course, the cube law is not valid up to $P = 2P_0$, which might be inferred from the presentation Eq. (33) by Shepherd et al. (1997).

Harris (1983) presents a different derivation of the cube law based on the so-called expansion factor of the gas mixture. The starting point is Eq. (5) where the dependence of burning velocity on pressure P and temperature T is neglected i.e. S_u is set equal to S_0. The mass of the burned gas m_b is written as the product of density ρ_b [kg/m^3] and volume V_b [m^3] of the burned gas.

$$\frac{dm_b}{dt} = \rho_b \frac{dV_b}{dt} + V_b \frac{d\rho_b}{dt} = A_f \rho_u S_0 \tag{34}$$

Applying the chain rule the derivative dV_b/dt can be written as

$$\frac{dV_b}{dt} = \frac{dV_b}{dr_b}\frac{dr_b}{dt} = A_f v_f \tag{35}$$

where v_f [m/s] is the flame speed with respect to a stationary observer. Inserting dV_b/dt from Eq. (35) into Eq. (34) and rearranging, one finds

$$v_f = \frac{\rho_u}{\rho_b} S_0 - \frac{V_b}{\rho_b A_f} \frac{d\rho_b}{dt} \tag{36}$$

At early stages of a confined explosion, the second term on the right hand side of Eq. (36) will be small compared to the first one and can be neglected. Then the relationship between the burning velocity S_0 and the flame speed v_f can be expressed simply as

$$v_f = \frac{\rho_u}{\rho_b} S_0 = ES_0 \tag{37}$$

Since it was assumed that the unburned and burned gases behave as ideal gases the expansion factor E can be expressed in terms of the temperatures T_0 and T_b and molar masses M_u and M_b [kg/mol] as

$$E = \frac{M_u}{M_b} \frac{T_b}{T_0} \tag{38}$$

Differentiating with respect to time and adding the ideal gas state equations of the unburned and burned gases, one finds (R is the gas constant 8.314 J mol^{-1} K^{-1})

$$\left(V_u + V_b\right) \frac{dP}{dt} + P\left(\frac{dV_u}{dt} + \frac{dV_b}{dt}\right) = R\left(\frac{T_0}{M_u}\frac{dm_u}{dt} + \frac{T_b}{M_b}\frac{dm_b}{dt}\right) \tag{39}$$

Because $V_u + V_b = V$ and $m_u + m_b = m$, Eq. (38) is simplified to

$$V\frac{dP}{dt} = R\left(\frac{T_b}{M_b} - \frac{T_0}{M_u}\right)\frac{dm_b}{dt} \tag{40}$$

Inserting dm_b/dt from Eq. (34), using the ideal gas state equation to express the density ρ_u and Eq. (38), one finds

$$V\frac{dP}{dt} = \frac{A_f S_0 P M_u}{T_0}\left(\frac{T_b}{M_b} - \frac{T_0}{M_u}\right) = A_f S_0 P\left(\frac{M_u}{M_b}\frac{T_b}{T_0} - 1\right) = \left(E - 1\right) A_f S_0 P \tag{41}$$

Assuming that the flame front is spherical with a radius of r_b that increases with the flame speed $v_f = ES_0$, Eq. (41) may be rewritten as

$$V\frac{dP}{dt} = \left(E - 1\right) 4\pi \left(ES_0 t\right)^2 S_0 P \tag{42}$$

Eq. (42) can be integrated by separation of variables

$$\int_{P_0}^{P}\frac{dP}{P}=E^2(E-1)\frac{4\pi S_0^3}{V}\int_0^t t^2dt \tag{43}$$

Integrating Eq. (43) and using Eq. (11), one finds

$$P=P_0\exp\left[\frac{E^2(E-1)\,4\pi(S_0t)^3}{3V}\right]=P_0\exp\left[E^2(E-1)\left(\frac{S_0t}{R_e}\right)^3\right] \tag{44}$$

For early stages of the explosion, the exponential function can be replaced by the first term in the power series and the cube law is obtained

$$\Delta P=P-P_0=P_0E^2(E-1)\left(\frac{S_0t}{R_e}\right)^3 \tag{45}$$

The two forms of the cube law differ in that the AICC pressure ratio P_m/P_0 in Eq. (33) is replaced by the expansion factor E in Eq. (45). Assuming ideal gases, the AICC pressure ratio can be expressed in a form similar to Eq. (38)

$$\frac{P_m}{P_0}=\frac{M_u}{M_b}\frac{T_m}{T_0} \tag{46}$$

The apparent discrepancy boils down to the value of burned gas temperature T_b used to calculate the expansion factor E in Eq. (38). Harris (1983) uses the adiabatic flame temperature in isobaric combustion T_{ad} [K], probably because this quantity is readily available in reference books. He also presents in tabular form adiabatic flame temperatures T_{ad} and expansion factors E calculated from these temperatures for hydrogen and several hydrocarbons.

On the other hand, in the derivation of Eq. (45) isochoric combustion is assumed and the maximum temperature in isochoric combustion T_m instead of the adiabatic flame temperature T_{ad} ought to be used for T_b. Thus, Eq. (33) is the correct form of the cubic law. Since T_m is always larger than T_{ad} the use of Eq. (45) will underestimate the overpressure ΔP somewhat.

3 APPLICATION OF PRESSURE RISE FORMULAS

The formulae derived in the preceding chapter will be applied to calculate the amount of hydrogen in a flammable mixture whose burning raises the overpressure in a room to the opening pressure of explosion relief panels. Two values of the opening pressure, 2 kPa and 3 kPa, will considered. With such low values of the opening pressure, only a small volume of hydrogen-air mixture around the ignition point is required to burn. Thus, it can be assumed that hydrogen concentration in this volume is constant. The concentration will be varied to cover the flammability range of hydrogen in air.

3.1 EXPANSION FACTOR OF HYDROGEN-AIR MIXTURE

The general combustion equation of one mole of hydrogen in dry air can be written as (Goodger 1977)

$$H_2 + m(O_2 + 3.76N_2) \rightarrow n_2H_2O + n_4H_2 + n_5O_2 + 3.76mN_2 \tag{47}$$

To simplify calculations, the inert gases Ar and CO_2 have been included in atmospheric nitrogen N_2. At lower temperatures, when the combustion products are not dissociated, the mole numbers are easily evaluated based on molar balance. The number of reactant moles is 1 + 4.76m. The number of product moles is denoted by n_b.

For lean mixtures, $m > 0.5$, $n_2 = 1$, $n_4 = 0$, $n_5 = m - 0.5$, $n_b = 0.5 + 4.76m$

$$H_2 + m(O_2 + 3.76N_2) \rightarrow H_2O + (m - 0.5)O_2 + 3.76mN_2 \tag{48}$$

For stoichiometric mixtures, $m = 0.5$, $n_2 = 1$, $n_4 = n_5 = 0$, $n_b = 2.88$

$$H_2 + 0.5(O_2 + 3.76N_2) \rightarrow H_2O + 1.88N_2 \tag{49}$$

For rich mixtures, $m < 0.5$, $n_2 = 2m$, $n_4 = 1 - 2m$, $n_5 = 0$, $n_b = 1 + 3.76m$

$$H_2 + m(O_2 + 3.76N_2) \rightarrow 2mH_2O + (1 - 2m)H_2 + 3.76mN_2 \tag{50}$$

At high temperatures, combustion products are partly dissociated and Eq. (47) is not necessarily valid. Coodger (1977) discusses the effect of dissociation on the adiabatic flame temperature T_{ad} of stoichiometric hydrocarbon-air mixtures. With hydrocarbon fuels generally, water vapour is dissociated to hydrogen H_2 and oxygen O_2, and carbon dioxide CO_2 to carbon monoxide CO and oxygen O_2. The effect of these reactions is to decrease T_{ad} by about 120 K. More extensive dissociation to atomic oxygen O and hydrogen H, and to radicals OH and NO, reduce T_{ad} by about 23 K.

Based on these conclusions, it seems reasonable to consider only dissociation of water vapour to H_2 and O_2 in the combustion of hydrogen in air. Then Eq. (47) is still valid. The equilibrium constant K for this dissociation reaction is (Goodger 1977)

$$\frac{P_{H_2O}}{P_{H_2}\left(P_{O_2}\right)^{1/2}} = K = \frac{n_2}{n_4\left(P_0\frac{n_5}{n_b}\right)^{1/2}} \tag{51}$$

where the number of product moles is $n_b = n_2 + n_4 + n_5 + 3.76m$. The temperature dependence of K is given by the Arrhenius equation

$$K = A\exp\left(-\frac{E_a}{RT}\right) \tag{52}$$

The coefficients A and E_a can found by fitting the values of K given by Goodger (1977): $A = 9.123 \cdot 10^{-4}$ atm$^{-1/2}$ and $E_a/R = 30\,300$ K. Alternatively, the temperature T corresponding to a given value of K is

$$T = \frac{\frac{E_a}{R}}{\ln \frac{A}{K}} \tag{53}$$

When dissociation of water vapour to H_2 and O_2 is considered, Eqs. (48) to (50) become (note that the number of hydrogen moles n_4 is small for lean mixtures and the number of oxygen moles n_5 is small for rich mixtures).

For <u>lean</u> mixtures, $m > 0.5$, $n_2 = 1 - n_4$, $n_5 = m - 0.5 + 0.5n_4$, $n_b = 0.5 + 0.5n_4 + 4.76m$

$$H_2 + m(O_2 + 3.76N_2) \rightarrow (1 - n_4)H_2O + n_4H_2 + (m - 0.5 + 0.5n_4)O_2 + 3.76mN_2 \tag{54}$$

For <u>stoichiometric</u> mixtures, $m = 0.5$, $n_2 = 1 - 2n_5$, $n_4 = 2n_5$, $n_b = 2.88 + n_5$

$$H_2 + 0.5(O_2 + 3.76N_2) \rightarrow (1 - 2n_5)H_2O + 2n_5H_2 + n_5O_2 + 1.88N_2 \tag{55}$$

For <u>rich</u> mixtures, $m < 0.5$, $n_2 = 2m - 2n_5$, $n_4 = 1 - 2m + 2n_5$, $n_b = 1 + n_5 + 3.76m$

$$H_2 + m(O_2 + 3.76N_2) \rightarrow (2m - 2n_5)H_2O + (1 - 2m + 2n_5)H_2 + n_5O_2 + 3.76mN_2 \tag{56}$$

The molar composition of the burned gases at a given temperature can be found by iteration as follows. Insert n_2, n_5 and n_b as functions of n_4 for lean mixtures or n_2, n_4 and n_b as functions of n_5 for rich mixtures in Eq. (51). Guess a value of n_4 for lean mixtures or n_5 for rich mixtures and calculate K. Calculate then the corresponding temperature T from Eq. (53). When the number of moles of product components n_i corresponding to given values of m and temperature T have been found by iteration, calculate the enthalpy difference

$$\Delta H = \sum_i n_i \Delta H_i = \sum_i n_i \int_{T_0}^{T} C_{pi} dT \tag{57}$$

where ΔH_i [J/mol] is the difference of enthalpy of component i between temperature T and reference temperature 25 °C, and C_{pi} [J/mol·K] is the specific heat capacity of component i at constant pressure. The temperature T_{ad} corresponds to the value where $\Delta H = 0$ and can be found by linear interpolation between the tabulated enthalpy values, as recommended by Goodger (1977).

The adiabatic flame temperatures of mixtures of hydrogen with dry air have been calculated using the enthalpy table in Goodger (1977). The molar ratio of oxygen and hydrogen in the unburned mixture m can be calculated noting that the hydrogen concentration C is

$$C = \frac{1}{1 + 4.76m} \tag{58}$$

Solving m from Eq. (58) one finds

$$m = \frac{\frac{1}{C} - 1}{4.76} \tag{59}$$

Insertion of the expressions for n_2, n_4 and n_b into Eq. (51) gives

$$K = \frac{m - n_5}{(0.5 - m + n_5)\left(P_0 \frac{n_5}{1 + 3.76m + n_5}\right)^{1/2}} \tag{60}$$

The results of the calculation without and with water vapour dissociation are presented in Table 1. Dissociation is significant only close to the stoichiometric concentration 29.6 %, where it results in a 96 K decrease of T_{ad}. For lean mixtures the dissociation product H_2 reacts with the surplus oxygen O_2, and for rich mixtures the dissociation product O_2 reacts with surplus hydrogen H_2.

Table 1. Adiabatic flame temperature T_{ad} [K] and expansion factor E for dry air

C, %	T_{ad}, no diss.	T_{ad}, diss.	Cantera	E, no diss.	E, diss.
8	941		944	3.03	
16	1546		1542	4.77	
24	2128	2123	2095	6.28	6.27
28	2420	2369	2323	6.98	6.86
29.6	2526	2430	2380	7.22	6.95
32	2458	2444	2387	7.08	7.04
40	2231		2210	6.54	
48	2003		1994	5.98	
56	1761		1762	5.35	
64	1518		1519	4.70	
72	1263		1264	3.99	

The calculated non-dissociated and dissociated adiabatic flame temperatures at stoichiometric concentration can be compared to those given by Goodger (1977). He gives the temperatures 2534 K and 2444 K. These are close to those in Table 1. However, the dissociated temperature calculated by him turns out to be slightly in error since he has used a value of 0.033 for n_5 instead of the correct value of 0.023.

Adiabatic flame temperatures have also been calculated with the Cantera code which considers also dissociation to atomic oxygen O and hydrogen H, and to radicals OH and NO. Comparison of the values in Table 1 shows that the simple method by Coodger (1977) overestimates the temperature by 57 K at 32 % hydrogen. On the other hand, practically the same temperatures are found both at the lean and rich limit.

Assume now that hydrogen is diluted with humid air to the concentration C. Denote the ratio of the partial pressure of water vapour to that of atmospheric oxygen by m_O. The reaction equations with no dissociation become:

For <u>lean</u> mixtures, $m > 0.5$, $n_2 = 1 + m_O m$, $n_4 = 0$, $n_5 = m – 0.5$, $n_b = 0.5 + (4.76 + m_O)m$

$$H_2 + m(O_2 + 3.76N_2 + m_O H_2O) \rightarrow (1 + m_O m)H_2O + (m – 0.5)O_2 + 3.76mN_2 \qquad (61)$$

For <u>stoichiometric</u> mixtures, $m = 0.5$, $n_2 = 1 + 0.5m_O$, $n_4 = n_5 = 0$, $n_b = 2.88+ 0.5m_O$

$$H_2 + 0.5(O_2 + 3.76N_2 + m_O H_2O) \rightarrow (1 + 0.5m_O)H_2O + 1.88N_2 \qquad (62)$$

For <u>rich</u> mixtures, $m < 0.5$, $n_2 = (2 + m_O)m$, $n_4 = 1 – 2m$, $n_5 = 0$, $n_b = 1 + (3.76 + m_O)m$

$$H_2 + m(O_2 + 3.76N_2 + m_O H_2O) \rightarrow (2 + m_O)mH_2O + (1 – 2m)H_2 + 3.76mN_2 \qquad (63)$$

When dissociation of water vapour to H_2 and O_2 is considered, Eqs. (61) to (63) become (note that the number of hydrogen moles n_4 is small for lean mixtures and the number of oxygen moles n_5 is small for rich mixtures).

For <u>lean</u> mixtures, $m > 0.5$, $n_2 = 1 + m_O m – n_4$, $n_5 = m – 0.5 + 0.5n_4$,
$n_b = 0.5 + 0.5n_4 + (4.76 + m_O)m$

$$H_2 + m(O_2 + 3.76N_2+ m_O H_2O) \rightarrow$$
$$(1 + m_O m - n_4)H_2O + n_4H_2 + (m – 0.5 + 0.5n_4)O_2 + 3.76mN_2 \qquad (64)$$

For <u>stoichiometric</u> mixtures, $m = 0.5$, $n_2 = 1 + 0.5m_O – 2n_5$, $n_4 = 2n_5$,
$n_b = 2.88 + 0.5m_O + n_5$

$$H_2 + 0.5(O_2 + 3.76N_2+ m_O H_2O) \rightarrow$$
$$(1 + 0.5m_O – 2n_5)H_2O + 2n_5H_2 + n_5O_2 + 1.88N_2 \qquad (65)$$

For <u>rich</u> mixtures, $m < 0.5$, $n_2 = (2 + m_O)m – 2n_5$, $n_4 = 1 – 2m + 2n_5$,
$n_b = 1 + n_5 + (3.76 + m_O)m$

$$H_2 + m(O_2 + 3.76N_2+ m_O H_2O) \rightarrow$$
$$[(2 + m_O)m – 2n_5)]H_2O + (1 – 2m + 2n_5)H_2 + n_5O_2 + 3.76mN_2 \qquad (66)$$

The molar ratio of oxygen and hydrogen in the unburned mixture m can be calculated noting that the hydrogen concentration C is

$$C = \frac{1}{1 + \left(4.76 + m_O\right)m} \tag{67}$$

Solving m from Eq. (67) one finds

$$m = \frac{\frac{1}{C} - 1}{4.76 + m_O} \tag{68}$$

Insertion of the expressions for n_2, n_4 and n_b into Eq. (51) gives

$$K = \frac{(1 + 0.5m_O)m - n_5}{(0.5 - m + n_5)\left(P_0 \frac{n_5}{1 + (3.76 + m_O)m + n_5}\right)^{1/2}} \tag{69}$$

Now the enthalpy of atmospheric water vapour at reference temperature 25 °C has to be subtracted from the enthalpy of burned gases in Eq. (57)

$$\Delta H = \sum_i n_i \Delta H_i - n_w H_{w0} = \sum_i n_i \int_{T_0}^{T} C_{pi} dT - n_w H_{w0} \tag{70}$$

where n_w is the number of moles of atmospheric water vapour per one mole of H_2 and H_{w0} is the enthalpy [J/mol] of water vapour at the reference temperature. In this case, $n_w = m_O m$.

Assume that the air relative humidity is 100 % at 298 K (26.85 °C). Water vapour partial pressure is 3.141 kPa and the ratio m_O is 0.152. The results of the calculation without and with water vapour dissociation are presented in Table 2. Dissociation is significant only close to the stoichiometric concentration 28.9 %, where it results in a 83 K decrease of T_{ad}.

The adiabatic flame temperatures and expansion factors for dry and humid air, respectively, are compared in Figs. 1 and 2. Dissociation is considered when appropriate. Air humidity decreases adiabatic flame temperature somewhat at rich mixtures. The decrease of T_{ad} has its largest value 67 K at 32 % hydrogen. At this concentration the expansion factor decreases from 7.04 to 6.88 or 2.3 %.

Table 2. Adiabatic flame temperature T_{ad} and expansion factor E for humid air

C, %	T_{ad}, no diss., K	T_{ad}, diss., K	E, no diss.	E, diss.
8	938		3.02	
16	1538		4.75	
24	2116	2110	6.25	6.23
28	2400	2345	7.15	6.79
28.9	2465	2382	7.07	6.88
32	2383	2377	6.89	6.88
40	2168		6.39	
48	1944		5.83	
56	1715		5.24	
64	1480		4.60	
72	1228		3.89	

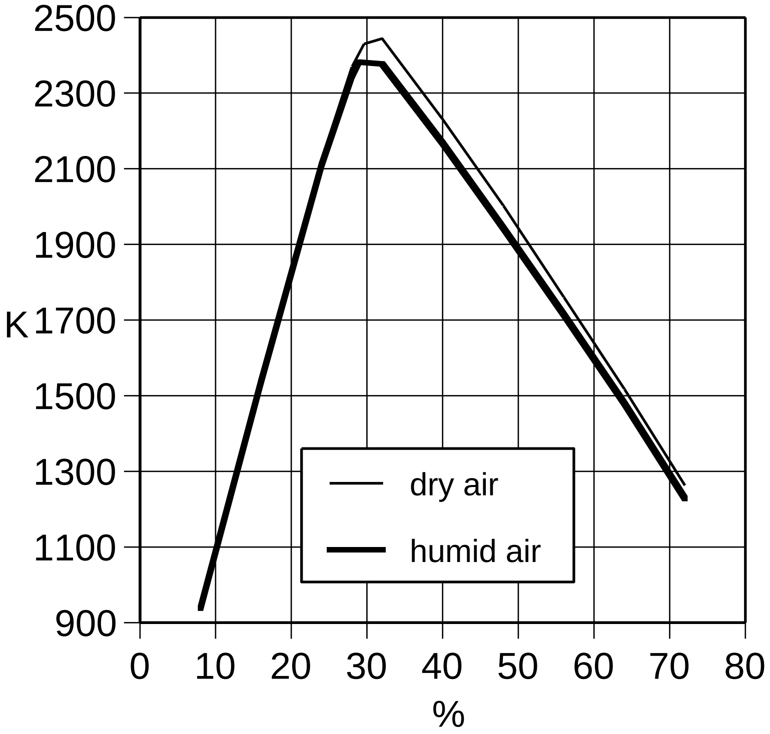

Figure 1. Adiabatic flame temperature of mixtures of hydrogen with dry and hydrogen with humid air (100 % RH at 298 K) burned at atmospheric pressure.

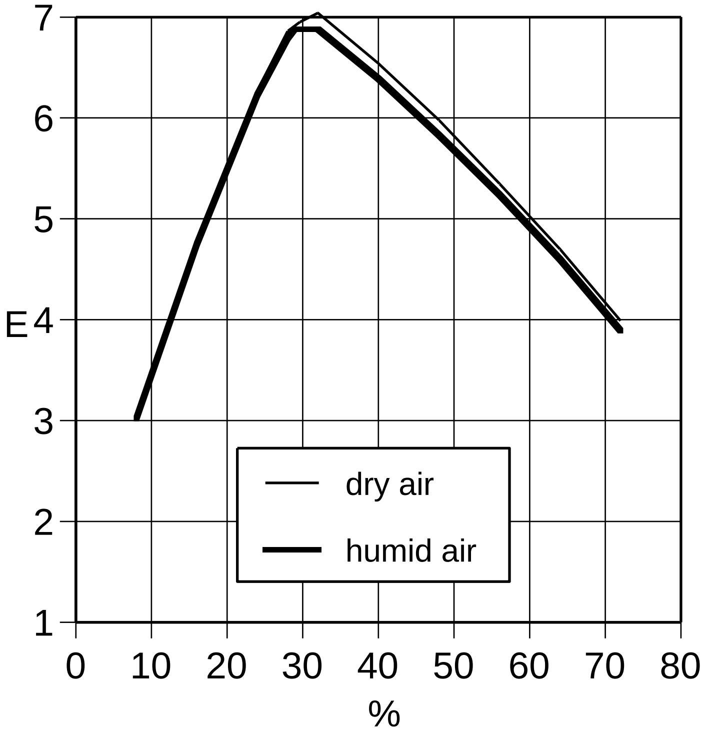

Figure 2. Expansion factor of mixtures of hydrogen with dry and humid air (100 % RH at 298 K) burned at atmospheric pressure.

3.2 AICC PRESSURE RATIO OF HYDROGEN-AIR MIXTURE

The AICC pressure ratio can be calculated in a similar way. Now the combustion occurs at constant volume and internal energy U [J/mol] remains constant during the process.

$$\Delta U = \sum_i n_i \Delta U_i - n_w U_{w0} = \sum_i n_i \int_{T_0}^{T} C_{vi}\, dT - n_w U_{w0} \qquad (71)$$

According to the definition of enthalpy U = H – Pv where v is the molar volume [m^3/mol]. Since all the gases involved are close to ideal gases, Pv ≈ RT and $C_{vi} \approx C_{pi}$ – R. Eq. (71) can be written as ($\Delta T = T - T_0$)

$$\Delta U = \sum_i n_i \left(\Delta H_i - R\Delta T\right) - n_w (H_{wo} - R\Delta T) = \sum_i n_i \int_{T_0}^{T} \left(C_{pi} - R\right) dT - n_w (H_{w0} - R\Delta T) \quad (72)$$

The enthalpy tables by Goodger (1977) have been used to calculate the AICC pressure ratio. The maximum temperature T_m corresponds to ΔU = 0 and is found by linear interpolation

The calculated values of maximum temperature T_m and AICC pressure ratio P_m/P_0 for different values of hydrogen concentration C can be compared to the results presented by Camp et al. (1983). However, the calculations by Camp et al. (1983) have been performed for a situation where the relative humidity for the mixture of hydrogen and air is 100 % at 298 K (26.85 °C).

In this case, the combustion equations are different from those derived above for hydrogen diluted by humid air. Denote the ratio of the partial pressure of water vapour to that of hydrogen by m_H. The reaction equations with no dissociation become:

For lean mixtures, m > 0.5, $n_2 = 1 + m_H$, $n_4 = 0$, $n_5 = m - 0.5$, $n_b = 0.5 + m_H + 4.76m$

$$H_2 + m(O_2 + 3.76N_2) + m_H H_2O \rightarrow (1 + m_H)H_2O + (m - 0.5)O_2 + 3.76mN_2 \qquad (73)$$

For stoichiometric mixtures, m = 0.5, $n_2 = 1 + m_H$, $n_4 = n_5 = 0$, $n_b = 2.88 + m_H$

$$H_2 + 0.5(O_2 + 3.76N_2) + m_H H_2O \rightarrow (1 + m_H)H_2O + 1.88N_2 \qquad (74)$$

For rich mixtures, m < 0.5, $n_2 = 2m + m_H$, $n_4 = 1 - 2m$, $n_5 = 0$, $n_b = 1 + m_H + 3.76m$

$$H_2 + m(O_2 + 3.76N_2) + m_H H_2O \rightarrow (2m + m_H)H_2O + (1 - 2m)H_2 + 3.76mN_2 \qquad (75)$$

When dissociation of water vapour to H_2 and O_2 is considered, Eqs. (73) to (75) become (note that the number of hydrogen moles n_4 is small for lean mixtures and the number of oxygen moles n_5 is small for rich mixtures).

For lean mixtures, $m > 0.5$, $n_2 = 1 + m_H – n_4$, $n_5 = m – 0.5 + 0.5n_4$,
$n_b = 0.5 + m_H + 0.5n_4 + 4.76m$

$$H_2 + m(O_2 + 3.76N_2) + m_H H_2O \rightarrow$$
$$(1 + m_H - n_4)H_2O + n_4H_2 + (m - 0.5 + 0.5n_4)O_2 + 3.76mN_2 \qquad (76)$$

For stoichiometric mixtures, $m = 0.5$, $n_2 = 1 + m_H – 2n_5$, $n_4 = 2n_5$,
$n_b = 2.88 + m_H + n_5$

$$H_2 + 0.5(O_2 + 3.76N_2) + m_H H_2O \rightarrow$$
$$(1 + m_H - 2n_5)H_2O + 2n_5H_2 + n_5O_2 + 1.88N_2 \qquad (77)$$

For rich mixtures, $m < 0.5$, $n_2 = 2m + m_H – 2n_5$, $n_4 = 1 – 2m + 2n_5$,
$n_b = 1 + m_H + n_5 + 3.76m$

$$H_2 + m(O_2 + 3.76N_2) + m_H H_2O \rightarrow$$
$$(2m + m_H - 2n_5)H_2O + (1 - 2m + 2n_5)H_2 + n_5O_2 + 3.76mN_2 \qquad (78)$$

The molar ratio of oxygen and hydrogen in the unburned mixture m can be calculated noting that the hydrogen concentration C is

$$C = \frac{1}{1 + 4.76m + m_H} \qquad (79)$$

Solving m from Eq. (79) one finds

$$m = \frac{\frac{1}{C} - 1 - m_H}{4.76} = \frac{1 - C_w - C}{4.76C} \qquad (80)$$

where the definition of $m_H = C_w/C$ has been inserted (C_w is the concentration of water vapour, in this case 3.1 %).

Insertion of the expressions for n_2, n_4 and n_b into Eq. (51) gives

$$K = \frac{m + 0.5m_H - n_5}{(0.5 - m + n_5)\left(P_0 \frac{n_5}{1 + 3.76m + m_H + n_5}\right)^{1/2}} \qquad (81)$$

The calculated maximum temperatures T_m for dry air, humid air and 100 % RH are given in Table 3 and the corresponding AICC pressure ratios in Table 4. Note that the stoichiometric hydrogen concentration depends on the water vapour concentration. Maximum temperatures are plotted in Fig. 3 and AICC pressure ratios in Fig. 4 for dry and humid air.

Table 3. Maximum temperatures T_m for isochoric combustion (K).

C, %	dry air		humid air		100 % RH	
	no diss.	diss.	no diss.	diss.	no diss.	diss.
8	1148		1141		1141	
16	1895		1881		1878	
24	2633	2564	2571	2541	2564	2536
28	2927	2804	2903	2773	2894	2764
28.7					2949	2784
28.9			2980	2774		
29.6	3058	2865				
32	2979	2900	2885	2837	2842	2805
40	2718	2717	2638	2635	2584	2583
48	2453		2379		2315	
56	2172		2114		2034	
64	1877		1829		1742	
72	1575		1532		1439	

Table 4. AICC pressure ratios.

C, %	dry air		humid air		100 % RH	
	no diss.	diss.	no diss.	diss.	no diss.	diss.
8	3.70		3.68		3.68	
16	5.85		5.80		5.80	
24	7.77	7.58	7.59	7.52	7.57	7.50
28	8.44	8.16	8.33	8.09	8.35	8.05
28.7					8.47	8.09
28.9			8.55	8.05		
29.6	8.74	8.30				
32	8.56	8.39	8.33	8.23	8.23	8.15
40	7.97	7.97	7.77	7.76	7.63	7.63
48	7.33		7.14		6.97	
56	6.61		6.46		6.23	
64	5.82		5.68		5.44	
72	4.97		4.84		4.57	

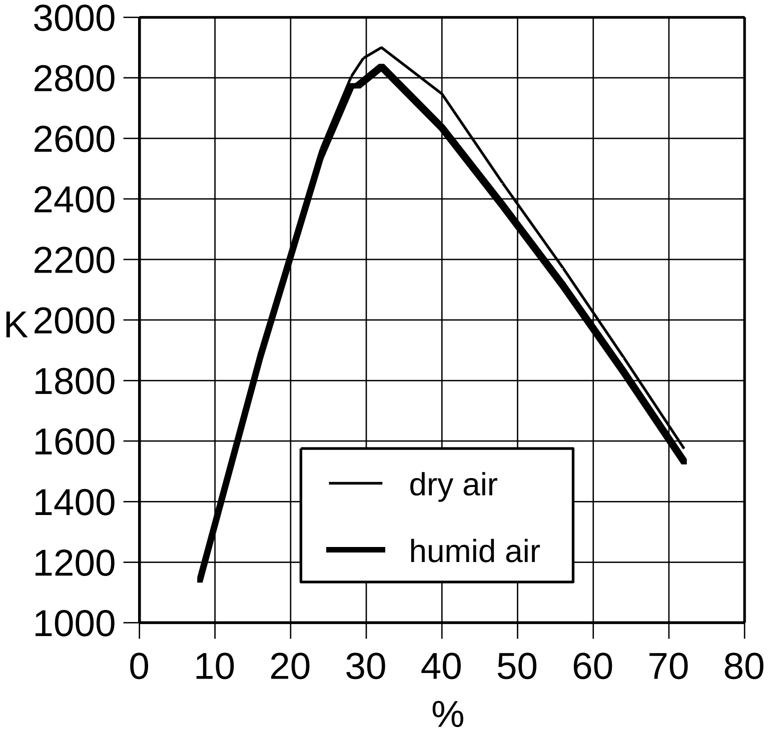

Figure 3. Maximum temperature of mixtures of hydrogen with dry and humid air (100 % RH at 298 K) burned at constant volume.

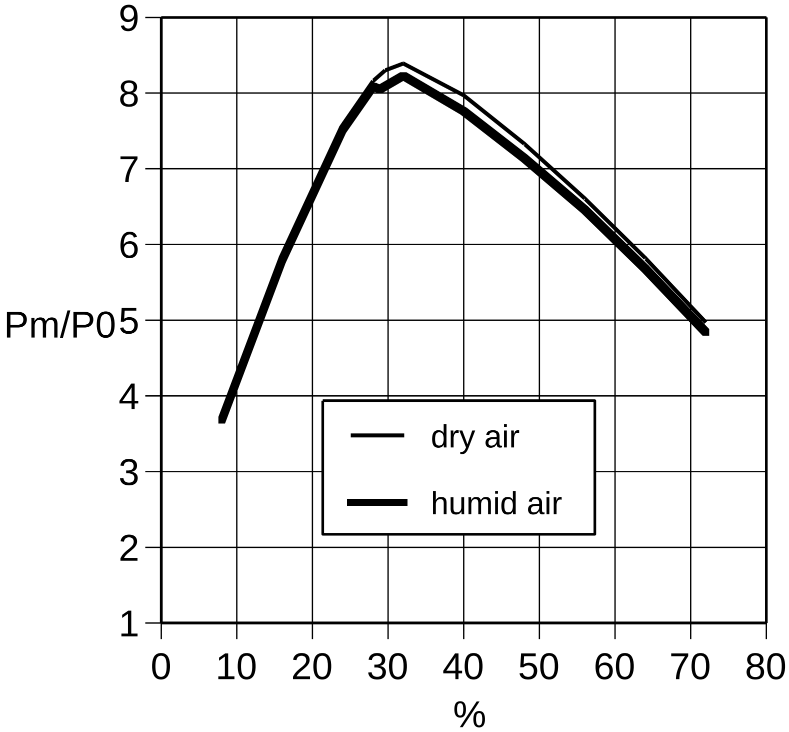

Figure 4. AICC pressure ratio of mixtures of hydrogen with dry and humid air (100 % RH at 298 K).

The calculated maximum temperatures T_m and AICC pressure ratios are compared to those presented by Camp et al. (1983) in Table 5 and Figs. 5 and 6.

Table 5. Maximum temperature and AICC pressure ratio for isochoric combustion at 100 % RH

C, %	calculated		Camp et al.	
	T_m, K	P_m/P_0	T_m, K	P_m/P_0
8	1141	3.68	1145	3.72
16	1878	5.80	1898	5.77
24	2536	7.50	2483	7.35
28	2764	8.05	2676	7.84
28,7	2784	8.09	2687	7.90
32	2805	8.15	2703	7.93
40	2583	7.63	2516	7.53
48	2315	6.97	2287	6.93
56	2034	6.23	2050	6.21
64	1742	5.44	1756	5.42
72	1439	4.57	1456	4.55

It is seen that the maximum temperatures and AICC pressure ratios calculated by the simple method by Goodger (1977) correspond to those given by Camp et al. (1983). In fact, the largest difference of temperatures is 102 K or 3.8 % at 32 % hydrogen. The temperatures presented by Camp et al. (1983) have been calculated with a numerical code that considers all dissociation processes. The present calculation included only the dissociation of water vapour to hydrogen and oxygen and was expected to overestimate T_m. The difference of the calculated AICC pressure ratios and those given by Camp et al. (1983) is no larger than 2.8 %. Thus the AICC pressure ratios calculated by this method can be applied to pressure rise calculations.

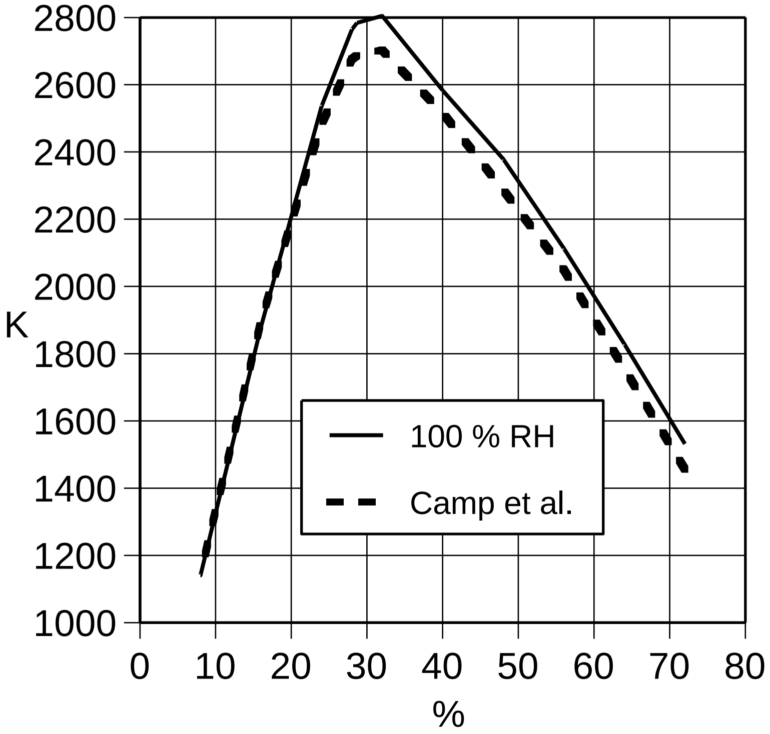

Figure 5. Maximum temperature for isochoric combustion at 100 % RH. Calculated temperatures are compared to those presented by Camp et al. (1983).

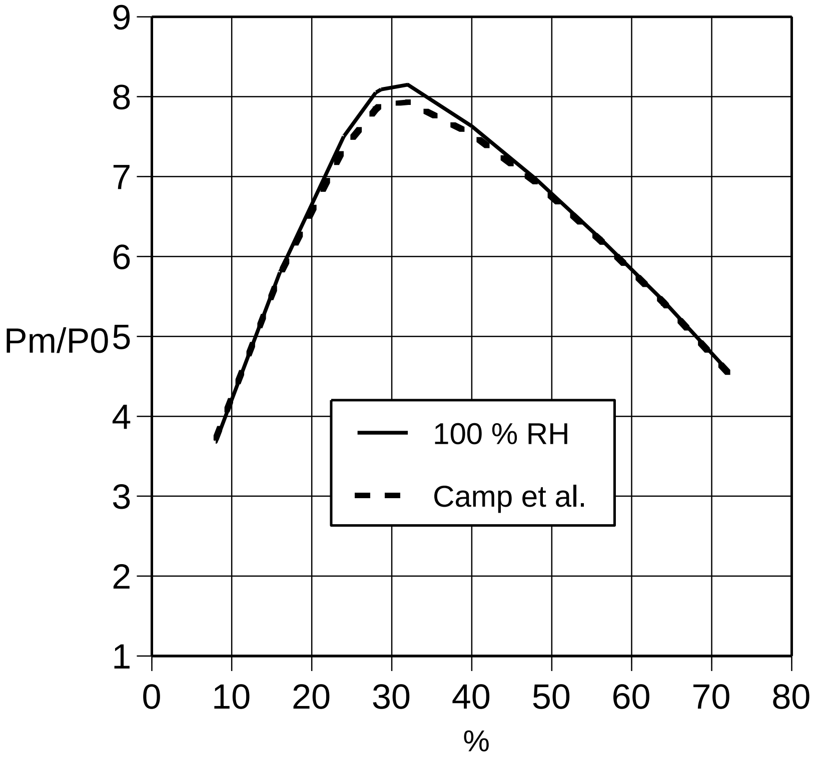

Figure 6. AICC pressure ratio at 100 % RH. Calculated pressure ratios are compared to those presented by Camp et al. (1983).

3.3 THE AMOUNT OF HYDROGEN

The amount of hydrogen in the part of the flammable mixture whose burning generates an overpressure ΔP in an enclosure of volume V is now calculated with the methods presented above. The simplest method is based on Eq. (2). The mass of hydrogen m_b can be solved from Eq. (2)

$$m_b = \frac{V\Delta P}{(\gamma - 1)h_c} \tag{81}$$

Insertion of $V = 1000\ m^3$, $\Delta P = 2000$ Pa, $\gamma = 1.4$ and $h_c = 120$ MJ/kg gives $m_b = 41{,}7$ g. The corresponding volume at $T_0 = 25$ °C and $P_0 = 1$ atm V_{H2} is 0.506 m^3. If water vapour dissociation is neglected, this value is valid for lean and stoichiometric mixtures, since all the hydrogen burns. When dissociation is considered the volume V_{H2} is

$$V_{H2} = \frac{0.506\ m^3}{n_2 - m_O m} \tag{82}$$

For rich mixtures, only part of the mixture burns and the volume V_{H2} is given by Eq. (82). The values of V_{H2} calculated from Eq. (82) are given in Table 6 and Fig. 7.

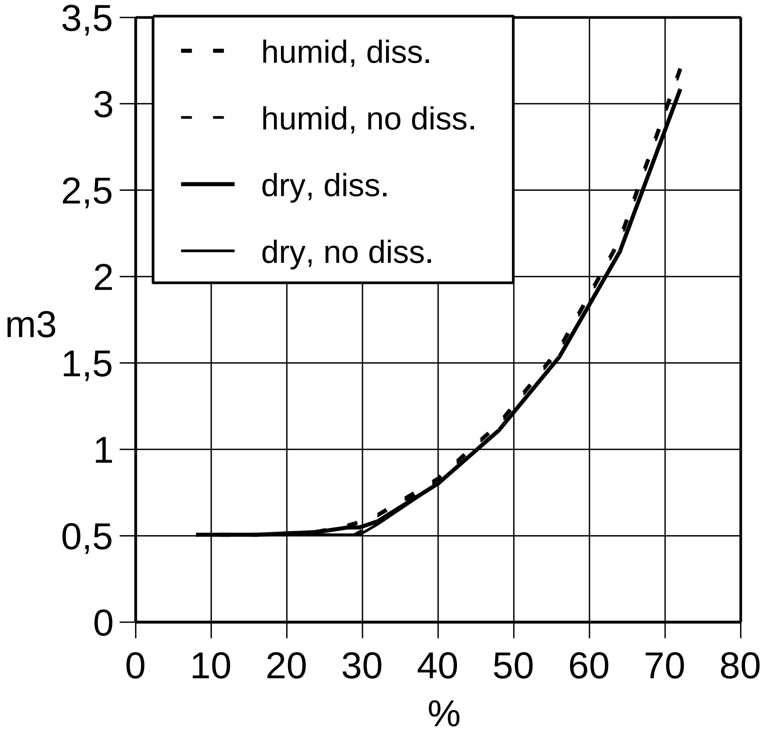

Figure 7. Hydrogen volume in the mixture whose burning generates a 2 kPa overpressure in a 1000 m^3 enclosure calculated from Eq. (82).

It is seen from Fig. 7 that the kink in the curves at stoichiometric concentration disappears when water vapour dissociation is considered. Otherwise the effect of dissociation on V_{H2} is small and can be neglected in most cases.

Table 6. Hydrogen volume [m^3] in the mixture whose burning generates a 2 kPa overpressure in a 1000 m^3 enclosure calculated from Eq. (81)

C, %	dry air		humid air	
	no diss.	diss.	no diss.	diss.
8	0.506		0.506	
16	0.506		0.506	
24	0.506	0.522	0.506	0.523
28	0.506	0.548	0.506	0.559
29.6/28.9	0.506	0.549	0.506	0.570
32	0.567	0.584	0.585	0.620
40	0.803	0.803	0.828	0.831
48	1.110		1.147	
56	1.534		1.581	
64	2.144		2.210	
72	3.085		3.203	

If only a part of the volume is filled with a rich mixture and there is no fuel outside this region, the combustion occurs in two phases. In the first phase, the combustion propagates as a spherical flame front. Only a part of the fuel burns, consuming all the oxygen in the rich mixture. This phase is called deflagration. In the second phase, air is mixed with the buoyant burned gases and the remaining fuel is combusted at a rate determined by the efficiency of the mixing process. There is no distinct flame front and no spherical symmetry. This phase is called fire ball. If there is enough air to burn all the fuel, the minimum mass of fuel required to generate the overpressure ΔP is given by Eq. (81).

When the amount of hydrogen calculated with Eq. (81) is compared with the results of other methods, only the first or deflagration phase has to be considered. In other words, it is assumed that the volume V is filled with a homogenous rich mixture, or in the partially filled case, the pressure rise during the fire ball phase is neglected. Thus, the volume V_{H2} will be calculated from Eq. (82).

Another method is based on Eq. (14). Eq. (14) can be modified to give the volume of burned gas V_b [m^3] at pressure P and temperature T_b

$$V_b = \frac{1-\left(\frac{P_0}{P}\right)^{1/\gamma}}{1-\left(\frac{P_0}{P_m}\right)^{1/\gamma}} V \tag{83}$$

Denote the volume of burned gas at pressure P_0 and temperature T_0 by V_{b0} [m^3]. Applying the ideal gas equation and inserting T_b from Eq. (9), one finds

$$V_{b0} = \frac{P}{P_0}\frac{T_0}{T_b}V_b = \frac{P}{P_0}\frac{T_0}{T_m}\left(\frac{P}{P_m}\right)^{\frac{1}{\gamma}-1} V_b \tag{84}$$

On the other hand, the temperature ratio T_0/T_m can be expressed in terms of the AICC pressure ratio, using Eq. (46).

$$\frac{T_0}{T_m} = \frac{M_u}{M_b}\frac{P_0}{P_m} = \frac{n_b}{n_u}\frac{P_0}{P_m} \tag{86}$$

Inserting Eq. (86) into Eq. (84), one finds

$$V_{b0} = \frac{P}{P_0}\frac{n_b}{n_u}\frac{P_0}{P_m}\left(\frac{P}{P_m}\right)^{\frac{1}{\gamma}-1} V_b = \frac{n_b}{n_u}\left(\frac{P}{P_m}\right)^{\frac{1}{\gamma}} V_b \tag{87}$$

Now the volume of burned hydrogen V_{H2} [m^3] can be had by dividing V_{b0} by n_b and noting that $1/n_u$ is equal to hydrogen concentration C in the unburned mixture

$$V_{H2} = \frac{1}{n_b}V_{b0} = \frac{1}{n_u}\left(\frac{P}{P_m}\right)^{\frac{1}{\gamma}} V_b = C\left(\frac{P}{P_m}\right)^{\frac{1}{\gamma}} V_b = C\left(\frac{P}{P_0}\right)^{\frac{1}{\gamma}}\left(\frac{P_0}{P_m}\right)^{\frac{1}{\gamma}} V_b \tag{88}$$

Finally, Eq. (83) is inserted into Eq. (88)

$$V_{H2} = \frac{\left(\frac{P}{P_0}\right)^{\frac{1}{\gamma}} - 1}{\left(\frac{P_m}{P_0}\right)^{\frac{1}{\gamma}} - 1} CV \tag{89}$$

The hydrogen volumes calculated from Eq. (89) are presented in Table 7. In Fig. 8 the values of V_{H2} in Table 7 are compared to those in Table 6 with water vapour dissociation considered. It is seen that Eq. (89) gives values that are up to 120 % larger than those calculated from Eq. (82). This is due to the fact that Eq. (9) gives values for the burned gas temperature T_b at the overpressure 2 kPa that are up to some 1000 K lower than the adiabatic flame temperature T_{ad}.

Table 7. Hydrogen volume [m^3] in the mixture whose burning generates a 2 kPa overpressure in a 1000 m^3 enclosure calculated using Eq. (88)

C, %	dry air		humid air	
	P_m/P_0	V_{H2}	P_m/P_0	V_{H2}
8	3.70	0.727	3.68	0.732
16	5.85	0.889	5.80	0.896
24	7.47	1.053	7.44	1.057
28	7.95	1.159	7.87	1.170
29.6/28.9	8.05	1.211	7.94	1.198
32	8.13	1.297	8.05	1.309
40	7.93	1.660	7.74	1.697
48	7.33	2.143	7.14	2.197
56	6.61	2.759	6.46	2.821
64	5.82	3.573	5.68	3.662
72	4.97	4.722	4.84	4.857

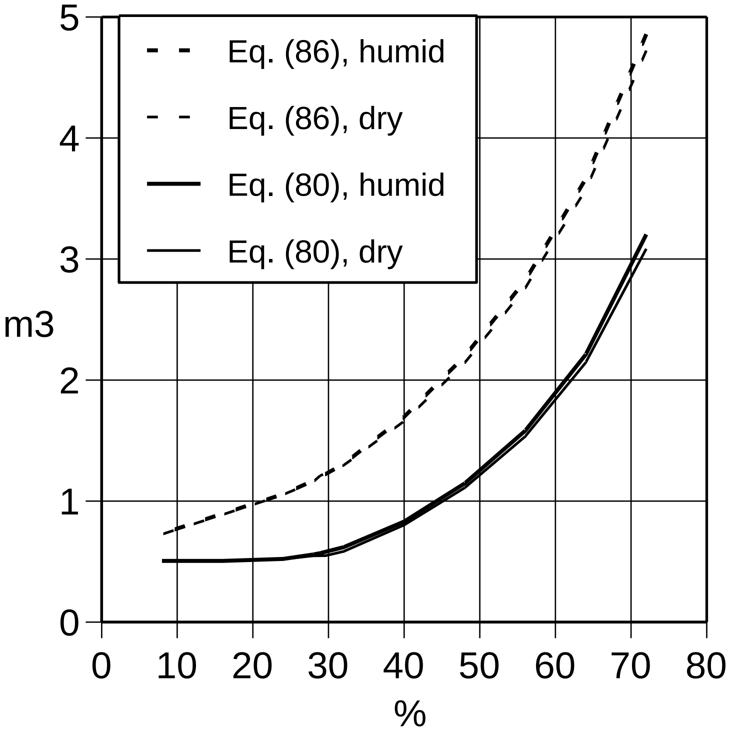

Figure 8. Hydrogen volume in the mixture whose burning generates a 2 kPa overpressure in a 1000 m^3 enclosure calculated using Eqs. (81) and (88).

Next, the hydrogen volume V_{H2} is calculated from equations derived from the isothermal approximation. Eq. (17) can be modified to give V_b

$$V_b = \frac{1 - \frac{P_0}{P}}{1 - \frac{P_0}{P_m}} V \tag{90}$$

The equation for V_{H2} can be derived in the same way as Eq. (88) or, simply, be setting $\gamma = 1$ in Eq. (89).

$$V_{H2} = \frac{P - P_0}{P_m - P_0} CV \tag{91}$$

The values of V_{H2} calculated from Eq. (91) are given in Table 8.

Table 8. Hydrogen volume [m^3] in the mixture whose burning generates a 2 kPa overpressure in a 1000 m^3 enclosure calculated using Eq. (90)

C, %	dry air		humid air	
	P_m/P_0	V_{H2}	P_m/P_0	V_{H2}
8	3.70	0.585	3.68	0.589
16	5.85	0.651	5.80	0.658
24	7.47	0.732	7.44	0.736
28	7.95	0.795	7.87	0.804
29.6/28.9	8.05	0.829	7.94	0.822
32	8.13	0.886	8.05	0.896
40	7.93	1.139	7.74	1.172
48	7.33	1.496	7.14	1.543
56	6.61	1.971	6.46	2.024
64	5.82	2.621	5.68	2.699
72	4.97	3.579	4.84	3.701

Another method based on the isothermal approximation uses the algebraic equations (24), (29) and the cube law Eq. (33). The time t required to generate an overpressure ΔP can be solved by iterating Eq. (24). However, because the chosen overpressure 2 kPa is small compared to P_0 the cube law can be used instead. A comparison of with Eq. (24) shows that error using the cube law Eq. (33) is no larger than 0.2 % in this case. The time t can be solved from Eq. (32)

$$t = \frac{1}{k}\left(\frac{\Delta P}{P_0}\right)^{1/3} \qquad (92)$$

The corresponding burned gas radius r_b can be found by iterating Eq. (29). The volume of burned hydrogen V_{H2} at T_0 = 25 °C and P_0 = 1 atm is then

$$V_{H2} = \left(1 + \frac{\Delta P}{P_0}\right)\frac{1}{n_b}\frac{T_0}{T_m}\frac{4\pi}{3}r_b^3 \qquad (93)$$

The temperature ratio T_0/T_m can be expressed in terms of the AICC pressure ratio

$$\frac{1}{n_b}\frac{T_0}{T_m} = \frac{1}{n_u}\frac{P_0}{P_m} = C\frac{P_0}{P_m} \tag{94}$$

Eq. (93) can be expressed in terms of the hydrogen concentration C and AICC pressure ratio

$$V_{H2} = C\left(1+\frac{\Delta P}{P_0}\right)\frac{P_0}{P_m}\frac{4\pi}{3}r_b^3 \tag{95}$$

The laminar burning velocity S_0 is needed to calculate the constant k defined by Eq. (19) for different hydrogen concentrations C. The values of S_0 are taken from Gelfand (2000) and are plotted in Fig. 9.

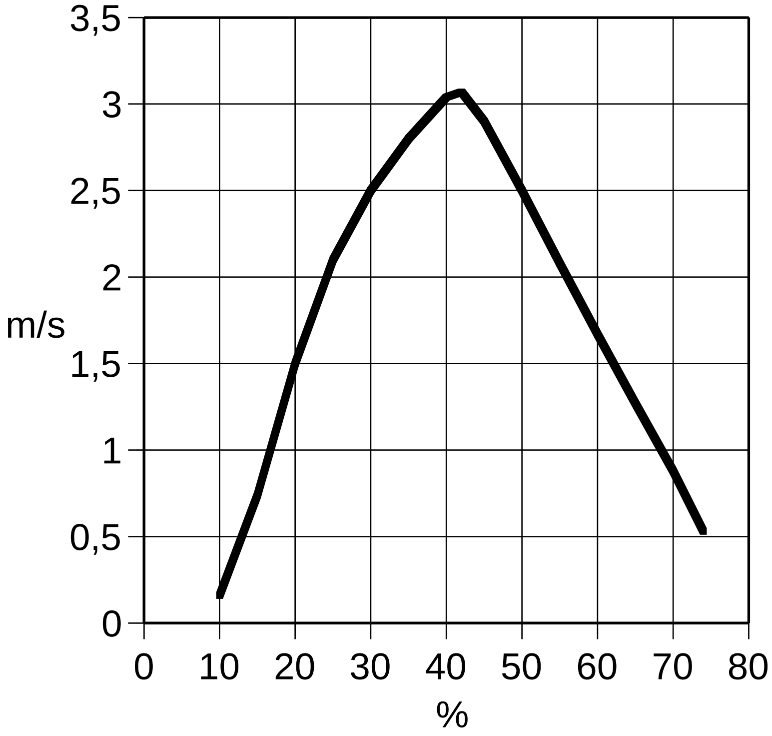

Figure 9. Laminar burning velocity of hydrogen (Gelfand 2000).

The calculated values of V_{H2} are presented in Table 9.

Table 9. Hydrogen volume [m^3] in the mixture whose burning generates a 2 kPa overpressure in a 1000 m^3 enclosure calculated using Eq. (95)

C, %	S_0, m/s	dry air		humid air	
		P_m/P_0	V_{H2}	P_m/P_0	V_{H2}
8	0.07	3.70	0.422	3.68	0.426
16	0.89	5.85	0.470	5.80	0.475
24	1.98	7.47	0.528	7.44	0.530
28	2.34	7.95	0.573	7.87	0.581
29.6/28.9	2.47	8.05	0.597	7.94	0.593
32	2.62	8.13	0.640	8.05	0.645
40	3.04	7.93	0.821	7.74	0.846
48	2.66	7.33	1.082	7.14	1.115
56	2.00	6.61	1.422	6.46	1.460
64	1.35	5.82	1.895	5.68	1.949
72	0.70	4.97	2.582	4.84	2.671

The values for isothermal approximation calculated from Eq. (91) and Eq. (95) are compared in Fig. 10. The hydrogen volumes V_{H2} calculated with the two adiabatic methods, Eqs. (82) and (89), and two isothermal methods, Eqs. (91) and (95) are compared in Fig. 11. Only the curves for dry air are shown in Fig. 11.

The most accurate results are given by Eq. (82) since this equation is based on thermodynamics only with no simplifying assumptions. This is taken as the reference method. The other adiabatic method of Eq. (89) gives values that are up to 120 % larger than those calculated from Eq. (82). As already noted, this is due to the fact that the burned gas temperature T_b calculated from Eq. (9) is in this case far too low: up to 1000 K lower than the adiabatic flame temperature.

The isothermal method of Eq. (91) gives up to 50 % larger values than Eq. (82). The more laborious isothermal method, Eq. (95), gives values that are the closest to those calculated with the reference method, Eq. (82). Eq. (95) underestimates the volume V_{H2} at rich mixtures (by 16 % at 72 % hydrogen) but deviates by no more than 10 % between 16 % and 56 % hydrogen concentration.

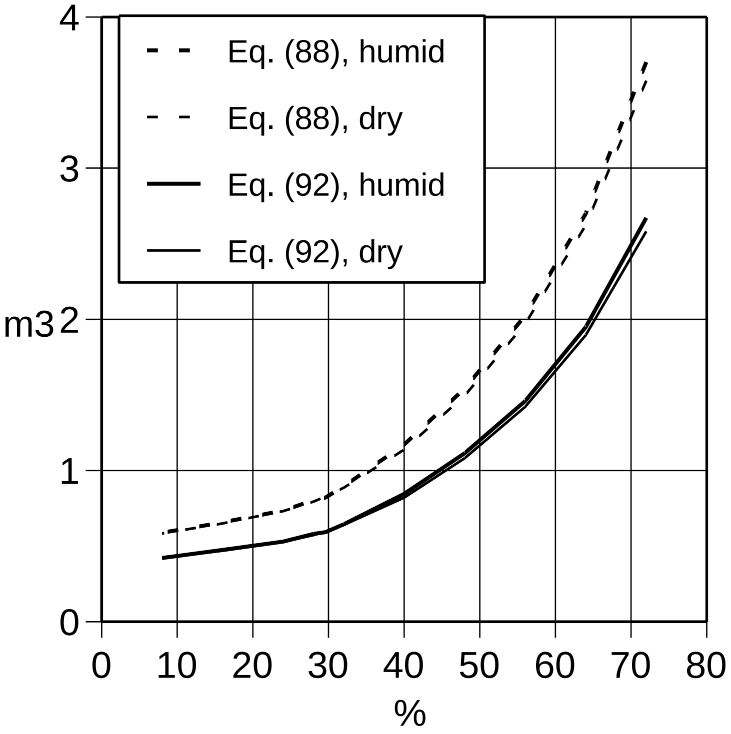

Figure 10. Hydrogen volume in the mixture whose burning generates a 2 kPa overpressure in a 1000 m^3 *enclosure calculated using Eqs. (91) and (95).*

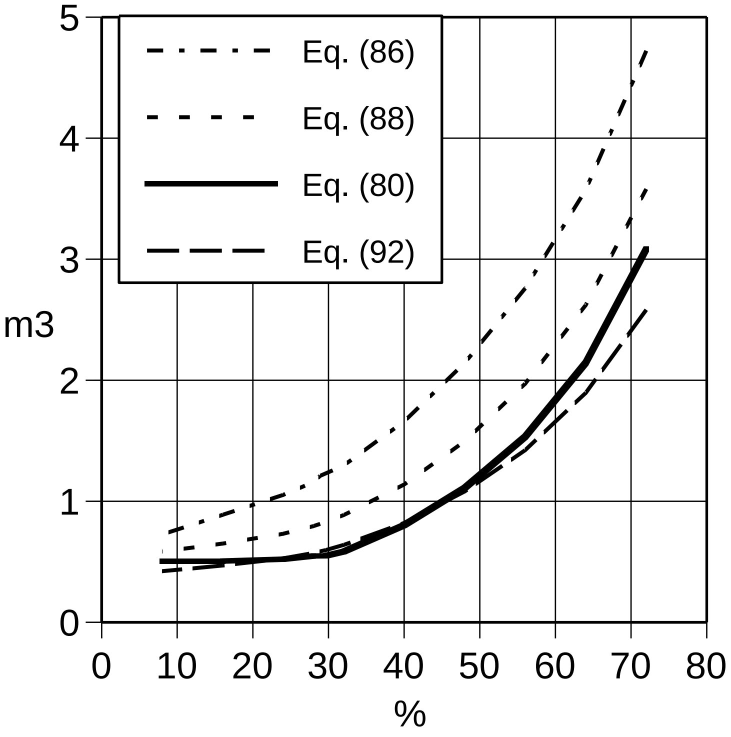

Figure 11. Hydrogen volume in the mixture with dry air whose burning generates a 2 kPa overpressure in a 1000 m^3 *enclosure calculated with two adiabatic methods, Eqs. (82) and (89), and two isothermal methods, Eqs. (91) and (95).*

Finally, the calculations are repeated for 3-kPa overpressure. Since Eqs. (82) and (91) are directly proportional to the overpressure, the hydrogen volumes V_{H2} are exactly 50 % larger than those calculated for 2-kPa overpressure. Eq. (89) gives 49.8 % and Eq. (95) 45 % larger values. The calculated hydrogen volumes are shown in Fig. 12. Fig. 12 is essentially similar as Fig. 11 with the volumes scaled by the factor 1.5. The curve calculated from Eq. (14) lies slightly lower.

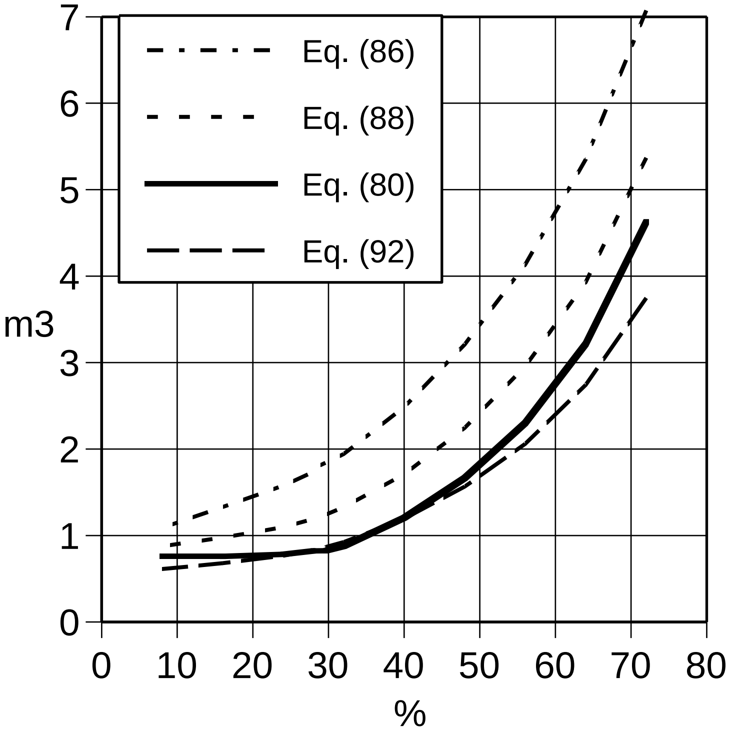

Figure 12. Hydrogen volume in the mixture with dry air whose burning generates a 3 kPa overpressure in a 1000 m^3 enclosure calculated with two adiabatic methods, Eqs. (82) and (89), and two isothermal methods, Eqs. (91) and (95).

4 SUMMARY

Simple methods to calculate pressure as a function of time in a confined explosion have been developed for the calculation of flame speed of a flammable mixture from measured pressure values. The basis of all simple models is conservation of energy for an adiabatic, constant volume system. For an ideal gas, the pressure at any time is directly proportional to the amount of burned gas.

The maximum pressure P_m is obtained when all of the gas is burned: The ratio P_m/P_0 (where P_0 is the initial pressure) is called AICC (Adiabatic Isochoric Complete Combustion) pressure ratio.

The rate of pressure rise dP/dt is directly proportional to the rate at which gas burns dm_b/dt. The latter is directly proportional to the product of flame area A_f and burning velocity S_u of the mixture. In real explosions turbulence develops in the unburned gas, distorting the flame front and increasing the product A_fS_u substantially. Engineering models usually treat turbulent flame propagation by replacing the burning velocity S_u with an effective "turbulent" value and interpreting the area A_f as the area of a smooth surface passing through the average location of the turbulent flame. There is no theory to predict turbulent burning velocity.

As the flame propagates through the enclosure, the pressure P increases uniformly in space, compressing both unburned and burned gases. This is a good approximation because the flame speed is small relative to the sound velocity.

For a given fuel concentration, the burning velocity S_u is dependent on both temperature and pressure. For engineering studies the ratio S_u/S_0 (where S_0 is the laminar burning velocity) is assumed to be proportional to T^2 and $P^{-\beta}$ where β is substance specific.

A differential equation for P can be derived neglecting turbulence effects, assuming equal specific heat ratios of unburned and burned gases and a spherical flame front. A similar differential equation can be derived for the flame front radius r_b. These equations, however, can be solved only numerically.

The differential equations can be simplified by making the so-called isothermal approximation. In this approximation the temperatures of the unburned and burned gases are constant and the pressure dependence of the burning velocity is neglected. The simplified differential equations are solved by separation of variables to yield a system of algebraic equations which can be solved by iteration to give P and r_b as functions of time.

The differential equation for P can integrated approximately by expanding the integrand as a power series. The result shows the experimental fact that the overpressure at early times is proportional to t^3. This is called the cube law.

Another derivation of the cube law gives a similar expression where the AICC pressure ratio is replaced by the expansion factor E (defined as the ratio of unburned and burned gases at ambient pressure). This due to the fact that adiabatic flame temperature in isobaric combustion has been used for the temperature of burned gas while the derivation above uses the maximum temperature in isochoric combustion.

Application of the formulae requires AICC pressure ratios for different concentrations of hydrogen. These were calculated for hydrogen mixed with dry and humid air. Also the expansion factors for these concentrations were calculated. The temperatures of burned gases were so high that dissociation of water vapour had to be considered.

The simple method used included only dissociation to hydrogen H_2 and oxygen O_2. A comparison with calculations using the Cantera code showed that this method overestimated the adiabatic flame temperature near the stoichiometric concentration. For lean mixtures the dissociation product H_2 reacts with the surplus oxygen O_2, and for rich mixtures the dissociation product O_2 reacts with surplus hydrogen H_2. Thus, near the lean and rich limit the method is accurate.

The method used to calculate the AICC pressure ratio was applied to the situation of hydrogen-air mixtures at 100 % relative humidity. The results were compared to those calculated with a combustion code that considers all dissociation processes. The AICC pressure ratios calculated assuming only water vapour dissociation were within 2.8 % of those calculated with a combustion code.

The formulae for pressure P and burned gas radius r_b were applied to calculate the amount of hydrogen in a flammable mixture whose burning raises the overpressure in a room to the opening pressure of explosion relief panels. The room volume was assumed to be 1000 m^3 and the opening pressure 2 kPa or 3 kPa.

The simplest and most accurate method was based on conservation of energy. Since this method required no approximations it was taken as the reference method. A formula based on the assumption of adiabatic dependence of the temperatures of unburned and burned gases on pressure overestimated the hydrogen volume by up to 120 %. A similar formula based on constant temperatures of unburned and burned gases overestimated the hydrogen volume by up to 50 %. The system of algebraic equations derived with the isothermal approximation gave values for the hydrogen volume that were closest to those calculated by the reference method. An increase of the opening pressure from 2 kPa to 3 kPa increased the hydrogen volumes exactly or nearly 50 %.

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