

# Correctness of Kinetic Data for Prediction of Multifront Detonation: Effect of Nitrogen (Part II)

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## 1 Introduction

In Part I of this paper, presented on this Colloquium, the results about prediction of cell size of multifront DW are presented. Two types of kinetic data for induction time  $\tau$  were used at calculation: the traditional Arrhenius

$$\tau = \frac{A \cdot \exp(E / RT)}{[f]^{k_1} [o]^{k_2} [in]^{k_3}}, \quad (1)$$

formula (1) for “averaged” kinetics, founded at approximation of experimental data, and the schema of detailed kinetics of combustible system. In formula (1)  $E$  is the activation energy of an «leading reaction» in an induction zone,  $R$  – universal gas constant,  $T$  – temperature in induction zone; in square brackets there is the concentration of a mixture components ( $f$  – fuel,  $o$  – oxidizer,  $in$  – inert gas),  $A$  and  $k_i$  – numerical factors (for example, [1]).

Unfortunately, as the “averaged”, as the detailed kinetic data for  $\tau$  demonstrate a pronounced scatter in the values of  $\tau$  for any fuels at extrapolation to the range of detonation parameters (temperature, density or concentration, and pressure). Moreover, even the “optimal” kinetic data, founded at best correlation of calculated and experimental cell sizes in dependence on pressure, temperature, dilution by argon or helium demonstrate the unusual behavior of cell size at dilution by nitrogen – experimental cell size exceeds the calculated value. The more nitrogen concentration the more distinction among experimental and calculated data. It is worth noting that according to the existing ideas, for almost all kinds of fuels, the role of nitrogen reduces only to that of an inert additive, and it is incorporated in (1) indirectly, via the variation of  $[O_2]$  in a mixture.

Formally, the situation with the faster increase in  $a(N_2)$  can be improved, for example, (a) by increasing the effective activation energy  $E$  (and by decreasing the  $A$ -coefficient for data binding with the starting point - “pure” mixture; (b) by increasing the order of the “limiting” reaction. Unfortunately, using this approach, it is necessary, for example, for the mixture  $H_2$ - $O_2$ - $N_2$ , either to “bring”  $E$  up to a value of 40 kcal/mole or to increase  $k_i$  above 2. Neither the first nor the second has sufficient physical substantiation or experimental support (although such “approaches” for other mixtures are known in the literature).

The effect of nitrogen dilution at calculation of  $\tau$  was taken into account mathematically in [2] with the use of a variable coefficient  $B$ , which characterizes the molar relations between nitrogen and oxygen in the mixture:  $[N_2]^n [O_2]^m = [N_2/O_2]^n [O_2]^{n+m} = B [O_2]^{n+m}$ . Attention should be given to the formal contradiction in formula (1), namely, to the trend of  $\tau$  to infinity as the concentration of any component decreases to zero. To avoid this mathematical feature in the extrapolation to the fuel-oxygen mixture (nonzero amount of  $N_2$  in the denominator of formula (1)), the coefficient  $B$  before  $[O_2]$  was defined via a fraction of the FOM in a nitrogen-diluted mixture rather than the molar fraction of  $N_2$ . For example, for a  $2H_2 + O_2 + nN_2$  mixture,  $B(n) = 3/(3+n)$  is added in the formula for  $\tau$  with  $k_1=k_3=0$ ,  $k_2=1$ ,  $A=5.38 \cdot 10^{-5}$ , and  $E = 17150$  cal/mole ( $H_2 - O_2$ ): at transition from a stoichiometric hydrogen-air mixture to a stoichiometric hydrogen-oxygen mixture, the value of  $B$  tends from  $3/6.76=0.444$  to a correct asymptotic limit, i.e., to  $3/3 = 1.0$ . Similarly,  $B(n) = 3.5/(3.5+2.5n)$  appears in the formula for  $C_2H_2 + 2.5O_2 + nN_2$  mixture -  $k_1=k_3=0$ ,  $k_2=1$ ,  $A = 2.82 \cdot 10^{-5}$ , and  $E=18100$  cal/mole;  $B(n) = 4/(4+3n)$  is introduced into the formula (1) for  $C_2H_4 + 3O_2 + nN_2$  -  $k_1=k_3=0$ ,  $k_2=1$ ,  $A = 3.55 \cdot 10^{-6}$ , and  $E=27500$  cal/mole; and  $B(n) = 3/(3+2n)$  appears in the formula of type (1) for  $CH_4 + 2O_2 + nN_2$  -  $k_1=k_3=0$ ,  $k_2=1$ ,  $A = 6.0 \cdot 10^{-6}$ , and  $E=33200$  cal/mole; etc. The concentration and  $\tau$  are given in moles per liter and microseconds, respectively [2].

## 2 Critical diameter of DW-diffraction and critical initiation energy in nitrogen containing mixture. The main results

Many important detonation parameters, which play the decisive role in explosion hazard problems, can be determined via the cell size  $a$  of multifront DW, which can be calculated using the models of detailed or "averaged" kinetics. Such parameters are the critical scales of gas charges, channel sizes for limiting propagation of detonation wave (DW), tube or channel sizes for DW-diffraction, critical initiation energies... In this paper the last two parameters are discussed. On Fig.1 the dependence of critical diameter for DW-diffraction  $d_{**}$  (mm) on initial pressure  $P_0$  (atm) is presented for mixture  $2H_2 + O_2$ : symbols – experimental data, solid line – calculated data with the help of formula (1) with "optimal" kinetic coefficients (without  $B$ -coefficient, of course). One can see the well correlation of experimental and calculated data.

Figs.2-5 gives the summary experimental data on the critical diameter for DW-diffraction upon dilution of typical stoichiometric fuel-oxygen mixtures (FOM) by nitrogen ( $p_0=0.1$  MPa,  $n$  is the molar concentration of  $N_2$  relative to  $O_2$ , and vertical lines refer to air:  $n=3.76$ ). The dashed curves are the calculated dependences  $d_{**}(N_2)$

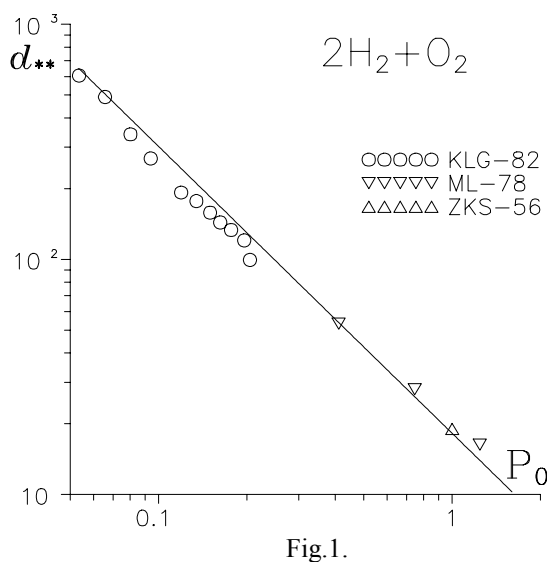


Fig.1.

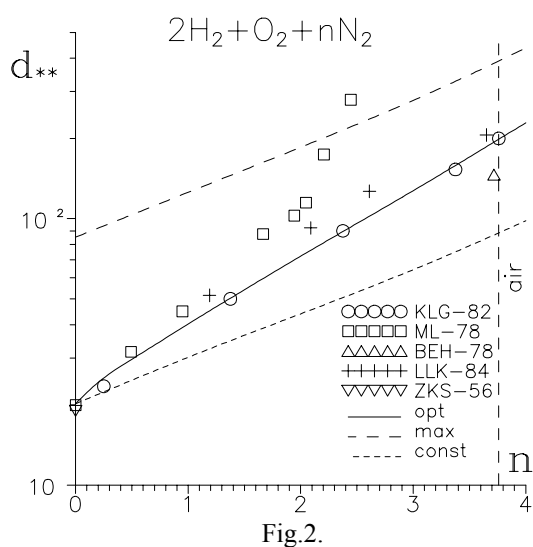


Fig.2.

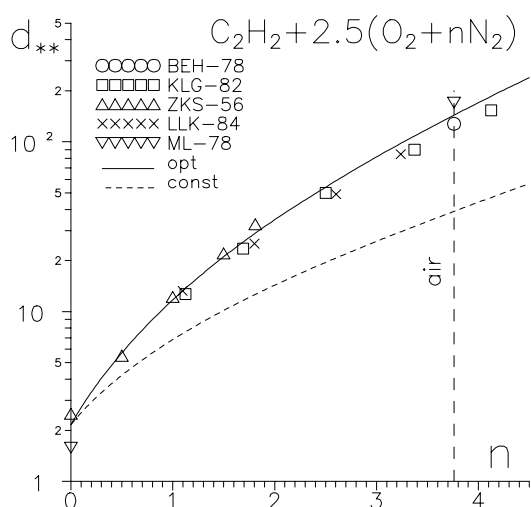


Fig.3.

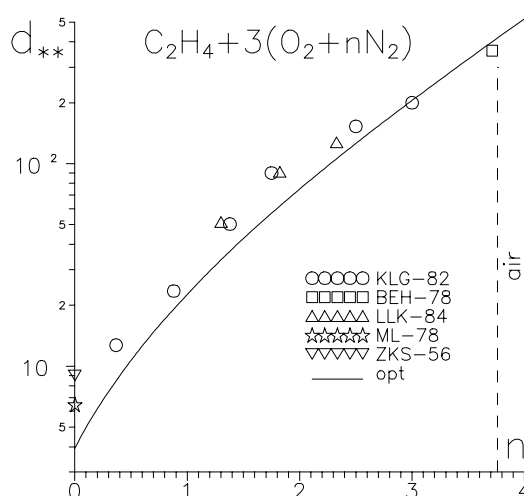


Fig.4.

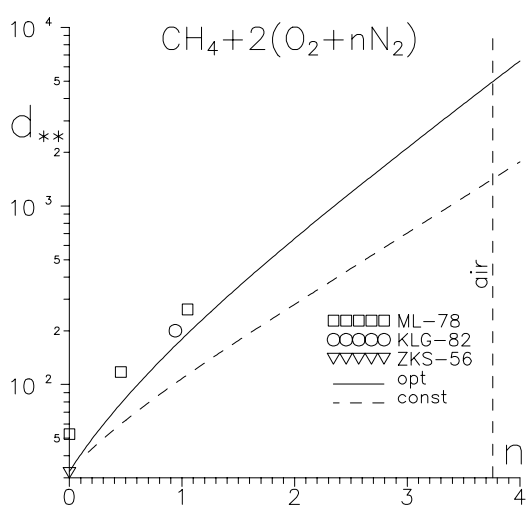


Fig.5.

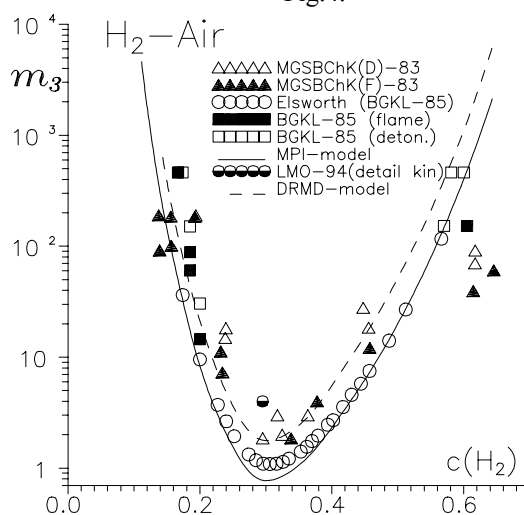


Fig.6.

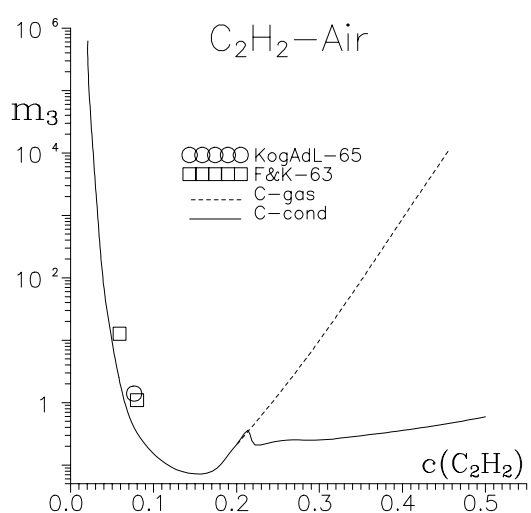


Fig.7.

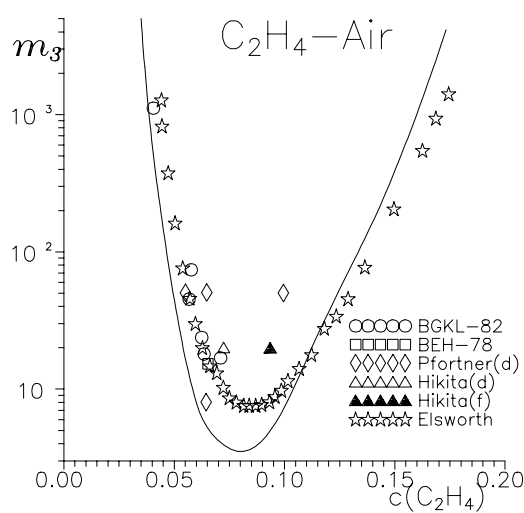


Fig.8.

within the averaged-kinetics model for the induction period  $\tau$  (Arrhenius type): lower dotted curve corresponds to the “optimal” coefficients of formula (1) for a FOM, upper - for “maximal” data.

The specific feature of diagrams is the more rapid increase of the experimental values of the critical diameter of DW-diffraction compared with the calculated values as the mixtures are diluted with nitrogen (likely similar dependence of cell size – part I [3]). As for cell size, the growing discrepancy among experimental and calculated data at  $n$  increase is not disappeared at replacement of the Arrhenius formula for “average” kinetic on the schema of detailed kinetic. The solid lines are the calculation data with the help of additional B-coefficients.

Figs.6-8 demonstrate the critical mass of HE-charge for initiation of spherical DW in typical fuel-air mixtures. One can see the correlation degree of experimental and calculated data.

The solid curves on Fig.1-8 refer to the calculation according to the corrected Arrhenius formula. Clearly, the refined technique for calculation of the ignition delays in presence of nitrogen in a mixture describes the experimental dependences  $f(N_2)$  much more correctly compared with the previously used ones.

It is possible to achieve the satisfactory correlation among the experimental and calculated data with the help of different sets of kinetic coefficients separately for fuel-oxygen (without nitrogen) and fuel-air mixtures, but the problem of selection of these data appears for mixtures, containing the different concentration of nitrogen. So, the reverse task – using the experimental results of cell size for determination of kinetic coefficients – seems more preferable in compared with data about ignition delay. Moreover, only integrated analysis of data file for different detonation parameters (cell size + critical diameter + critical energy + ...) can allow to define the correct kinetic coefficients for detonation conditions.

### 3 Conclusion

A faster increase in the critical diameter of DW-diffraction and the critical initiation energy compared with that predicted by the traditional kinetic calculations has been shown for nitrogen-diluted fuel-oxygen mixtures of hydrogen and typical hydrocarbons. Dilution of mixtures with other inert gases does not lead to a similar effect. Only integrated analysis of data file for different detonation parameters (cell size + critical diameter + critical energy + ...) can allow to define the correct kinetic coefficients for detonation conditions.

### 4 Acknowledgment

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