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

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1 Introduction

The strong spatial and time nonuniformity of the local parameters of multifront DW makes it practically impossible to perform reliable experimental measurements of the detailed kinetics of chemical reactions occurring in the detonation wave (DW). So the greater part of the kinetics measurements were performed under uniform conditions («averaged» parameters), which are typical for shock waves. Such measured results (obtained under conditions which be different from the detonation ones) then were extrapolated (with any degree of accuracy) to the range of detonation conditions.

Mostly, the experimental data of "averaged" induction time τ for combustible system are approximated with

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

the help of Arrhenius formula (1), where 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, the "averaged" kinetic data for τ obtained by various researchers demonstrate a pronounced scatter in the values of τ for any fuels at extrapolation to the range of detonation parameters (temperature, density or concentration, and pressure).

The Arrhenius formula is simple formula for engineering estimation of τ and at numerical 2-D calculation. Another way to receive the answer on question about induction time is connected with schema of detailed kinetics, widely investigated in latest time. The answer can be ascertained from formal points of view after solution of complete (or correctly short-cut) equations system for rates of each-possible elementary reactions at transformation of an initial system into products. In an ideal, after a numerical solution of a similar system it is possible to analyze the character of modification of an induction period (by defiining it, for example, on a maximum rate of temperature increase) and of reaction zone.

Unfortunately, the available inaccuracy in numerical values for rates of elementary reactions in the range of parameters typical for combustion and detonation allows to analyze only qualitative modification of induction time profiles without guarantees of their quantitative correspondence to experimental values.

2 Prediction of cell size in nitrogen containing mixture. The main results

Many important detonation parameters, which play the decisive role in explosion hazard problems, such as critical initiation energies, critical scales of gas charges, channel sizes for limiting propagation of detonation wave (DW), tube or channel sizes for DW-diffraction, etc. can be determined via the cell size a of multifront DW. In turn, the value of a can be calculated using the models of detailed or "averaged" kinetics. On Fig.1 the dependence of cell size a (mm) on initial pressure P_0 (atm) is presented for mixture $2H_2+O_2$: symbols – experimental data, solid and dashed lines – calculated data with the help of formula (1) of different authors (from
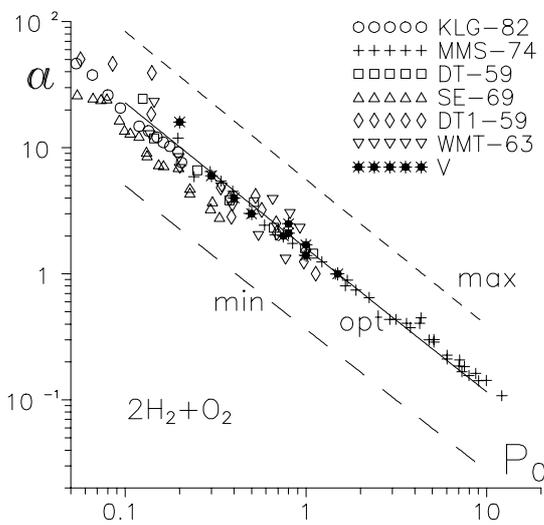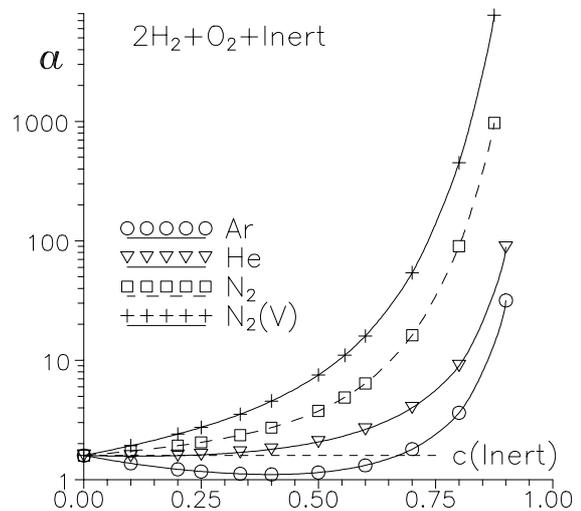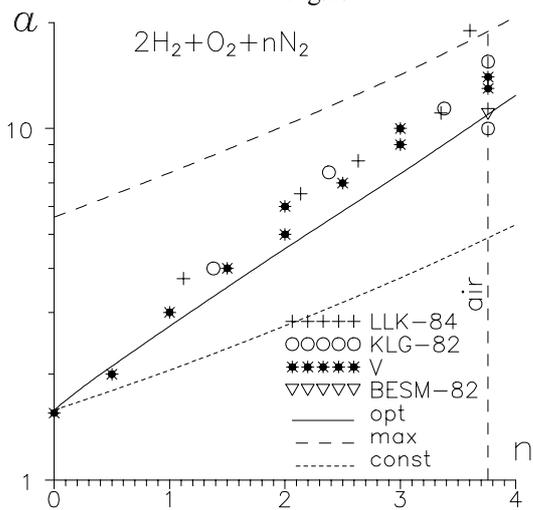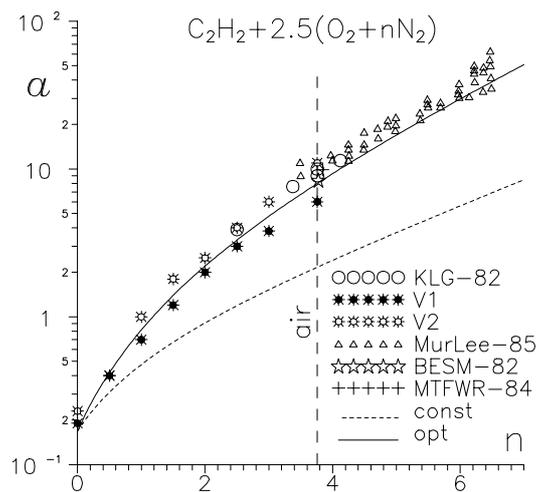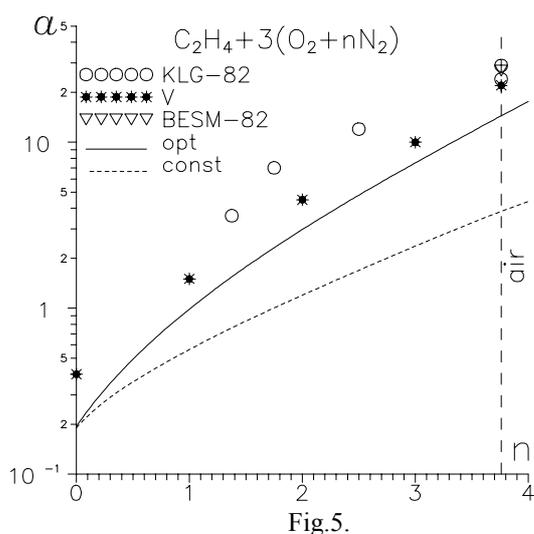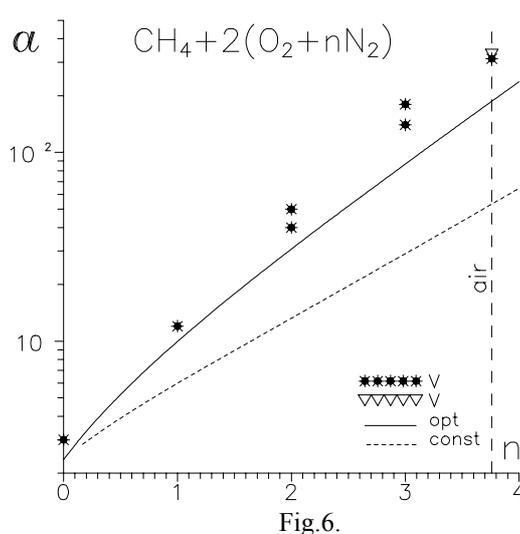

Fig.1.

Fig.2.

Fig.3.

Fig.4.

Fig.5.

Fig.6.

minimal up to maximal values of τ at detonation conditions, including the optimal kinetic data). The main conclusion of this graph is well correlation of experimental data with predicted.

On Fig.2 the calculated dependence of cell size a (mm) on molar concentration of inert gas c(inert) is presented for mixture $2H_2+O_2+nIn$ (three lines with first symbols of argon, helium and nitrogen were calculated with "optimal" kinetic data of Arrhenius formula as on Fig.1). Argon demonstrates the U-form of $a(c_{inert})$ dependence, lines for He and N_2 are increased with c.

Figs.3-5 gives the summary experimental data on the cell size of a multifront DW 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 $a(N_2)$ within the framework of the averaged-kinetics model for the induction period τ (Arrhenius type): only the curves which correspond to the "optimal" choice of the coefficients of formula (1) for a FOM are presented:

$H_2 - O_2$: $k_1=k_3=0$, $k_2=1$, A=5.38 10^{-5}, and E = 17150 cal/mole;
$C_2H_2 - O_2$: $k_1=k_2=0.5$, $k_3= 0$, A =2.82 10^{-5}, and E=18100 cal/mole;
$C_2H_4 - O_2$: $k_1=k_3=0$, $k_2=1$, A =3.55 10^{-6}, and E=27500 cal/mole;
$CH_4 - O_2$: $k_1=k_3=0$, $k_2=1$, A =6.0 10^{-6}, and E=33200 cal/mole;
the concentration and τ are given in moles per liter and microseconds, respectively [2].

The specific feature of diagrams is the more rapid increase of the experimental values of the cell size compared with the calculated values as the mixtures are diluted with nitrogen. Similar tendency is typical also for another mixtures (propane,...) and for another characteristic parameters of multifront detonation with the dimension of length (or proportional to a) [2]: critical diameter of a free gas charge, channel sizes for limiting DW propagation, critical initiation energy, critical diameter of DW-diffraction…(part II of this paper)

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. For example, at dilution of a stoichiometric hydrogen-oxygen mixture by nitrogen and transition to a hydrogen-air mixture (N_2/O_2=3.76), the τ value increases by a factor of 9 (the calculated delay was determined as the period from the beginning of the process to the moment of fastest growth in temperature). At the same time, a calculation by means of formula (1) for the averaged kinetics shows that none of the known sets of kinetic constants for (1) gives the same increase for the "averaged'" induction period [2]. Owing to this, the curves $a(N_2)$, which were calculated according to the delays from the detailed kinetics model, are somewhat steeper than the curves which correspond to the averaged kinetics, although they are lower than the experimental ones as befor.

Moreover, using of schema of detailed kinetic for prediction of detonation cell size at 2-D calculation demonstrates that calculated size is smaller experimental. For example, on 20-ICDERS the authors of [3] demonstrated the calculated 3-D spinning DW in tube of 1 mm diameter at P_0=0.1 MPa, which was calculated with the help of detailed kinetic data for hydrogen-air mixture. But at experiment the spinning DW for this mixture is observed in tube with diameter about 5 mm. In tube of diameter 1 mm spinning DW is impossible!

It is necessary to emphasize that as the mixtures are diluted, the unusual behavior of the cell size (and the other parameters proportional to *a*) is observed only for nitrogen. At this, the experimental dependences $a(N_2)$ do not go beyond the limits calculated with the use of the "minimum" and "maximum" (for example, upper dotted curve on Fig.3) delays, displacing toward the upper boundary as the content of N_2 in the mixture grows. For the mixtures with argon or helium, the experimental values of a(Ar, He) are in agreement with the calculated ones up to very high concentrations of an inert gas, which markedly exceed the nitrogen concentration in stoichiometric fuel-air mixtures.

3   Correction of Arrhenius formula coefficients for nitrogen containing mixture

The effect of nitrogen dilution at calculation of τ 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: $[N_2]^n [O_2]^m = [N_2/O_2]^n [O_2]^{n+m} = B [O_2]^{n+m}$.

The solid curves on Fig.3-6 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 $a(N_2)$ much more correctly compared with the previously used ones.

4   Conclusion

A faster increase in the cell size and other very important multifront detonation parameters compared with that predicted by the 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. Correction of the kinetics data is required for calculation the ignition delays of various nitrogen-containing mixtures for detonation conditions.

5   Acknowledgment

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