

# Skeletal mechanism construction by entropy production analysis: detailed reaction mechanisms with irreversible reactions

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## Introduction

The combustion technologies nowadays adopted to reduce pollutant emissions and increase combustion efficiency are complex and their accurate description requires complex reaction mechanisms consisting of hundreds of species and several thousands of reactions [1]. However, especially in application to practical systems, numerical simulations can be afforded only adopting simplified descriptions of the kinetics. Therefore, the possibility to obtain reduced mechanisms with assessed range of validity is an important topic.

Kooshkbaghi et al. [2,3] proposed to identify the most relevant reactions in a detailed chemical mechanism evaluating the entropy generated by the elementary reactions, thus obtaining an attractive approach for mechanism reduction. This approach allows to identify, with a simple analysis of thermodynamic states crossed during the chemical transformation of reactants to products, the most relevant reactions, thus deriving skeletal mechanisms which only include the most significant species for a particular application. Being based on thermodynamic law, the degree of approximation can be selected and verified.

In the original formulation [2], the evaluation of the entropy production rate was based on the principle of detailed balance, a property that does not hold in the case of irreversible reactions which are often adopted in the development of detailed mechanisms for complex fuels (e.g. [4]). Therefore, it is advisable to have a more general formulation that holds even in presence of irreversible reactions. In this work the recent advances of this research effort [5,6] are presented: starting from the principles of chemical reaction thermodynamics, an alternative formulation is derived valid for both reversible and irreversible reactions and thus useful for the reduction of a wide set of detailed mechanisms.

To illustrate the potentiality of this approach, it has been applied to obtain the reduction of the detailed mechanism developed by the group of CRECK [4], formed prevalently by irreversible reactions, to derive a reduced mechanism for n-dodecane.

## Thermodynamics and entropy related functions

The second law of thermodynamics postulates the existence of a state function, called entropy [7]. Entropy is an extensive property. If a system consists of several parts, the total entropy is equal to the sum of the entropies of each part. The change of entropy  $dS$  can be split into two contributions. Denoting by  $dS_{ext}$  the contribution due to interactions with the exterior, and by  $dS_{int}$  the contribution due to changes inside the system, we have:

$$dS = dS_{ext} + dS_{int}$$

Expressing entropy as a function of internal energy  $U$  (neglecting any other contribution to the total energy), volume  $V$  and number  $n$  of moles [7], its differential is given by:

$$dS = \frac{1}{T} dU + \frac{P}{T} dV - \frac{1}{T} \sum_{k=1}^{N_S} \mu_k dn_k$$

where the definitions of absolute temperature, pressure and chemical potentials [8] have been used [5,6]. When chemical reactions occur, the mole number  $n_k$  of the  $k$ -th species may change both by mass addition from outside and by chemical reaction inside the control volume [8]  $dn_k = dn_{ext,k} + dn_{int,k}$  where  $dn_{ext,k}$  and  $dn_{int,k}$  represent the external (due to exchange with the surrounding) and the internal (due to chemical reactions) differential change of the moles of the  $k$ -th species. The focus in this work is on the internal contribution to entropy production  $dS_{int}$ , given by:

$$dS_{int} = -\frac{1}{T} \sum_{k=1}^{N_S} \mu_k dn_{int,k}$$

due only by chemical reactions, being all other terms in entropy production due to external interactions [5,6]. The rate of change of the moles of the  $k$ -th species due to chemical reactions can be given in terms of production rates [8]:

$$\frac{dn_{int,k}}{dt} = V \sum_{j=1}^{N_R} (v_{kj}^P - v_{kj}^R) (q_j^f - q_j^r)$$

where  $v_{kj}^P$  and  $v_{kj}^R$  are the stoichiometric coefficients on the products and reactants side of the  $j$ -th reaction and the  $q_j^f$  and  $q_j^r$  are the forward and reverse rate of progress of the  $j$ -th elementary reaction respectively. Thus:

$$\frac{dS_{int}}{dt} = -\frac{V}{T} \sum_{k=1}^{N_S} \mu_k \sum_{j=1}^{N_R} (v_{kj}^P - v_{kj}^R) (q_j^f - q_j^r)$$

Using the chemical affinity (or De Donder's affinity) of the  $j$ -th reaction [8]:

$$a_j = -\sum_{k=1}^{N_S} \mu_k (v_{kj}^P - v_{kj}^R) \quad (1)$$

we can express the rate of change of entropy due to chemical reactions in the form:

$$\frac{dS_{int}}{dt} = -\frac{V}{T} \sum_{j=1}^{N_R} a_j (q_j^f - q_j^r)$$

### Entropy analysis

We define the relative contribution of each reaction to the total internal entropy production as:

$$r_j = \frac{dS_{int,j}/dt}{dS_{int}/dt} = \frac{a_j (q_j^f - q_j^r)}{\sum_{j=1}^{N_R} a_j (q_j^f - q_j^r)} \quad (2)$$

In the absence of deviations from the principle of detailed balance, the chemical affinity can be given in terms of production rates [7] as  $a_j = RT \ln(q_j^f/q_j^r)$ . The relative contribution of each reaction to the total (internal) entropy production can be written as [2]:

$$r_j = \frac{\ln(q_j^f/q_j^r) (q_j^f - q_j^r)}{\sum_{j=1}^{N_R} \ln(q_j^f/q_j^r) (q_j^f - q_j^r)} \quad (3)$$

It is explicitly observed that the validity of the principle of detailed balance imply the positivity of entropy production for each reaction in the scheme. However, reaction mechanisms often violate the principle of detailed balance. This is, indeed, the case when many reactions are defined as irreversible elementary reactions or when the reverse rates that would normally be computed through the equilibrium constant are specified separately (see, for instance, the REV flag in CHEMKIN format [9]). However, adopting the general expression of Eq. (2), negative values of  $r_j$  can arise for some reactions, but the total entropy production is always positive [10]. We are interested to all reactions that mainly contribute, both positively and negatively, to establish the entropy balance of the entire mechanism. Therefore, the measure of the importance of each reaction is defined by the expression:

$$\mathcal{R}_j = \frac{|a_j(q_j^f - q_j^r)|}{\sum_{j=1}^{N_R} |a_j(q_j^f - q_j^r)|} \quad (4)$$

In Eq. (4) an important role is played by the chemical affinity  $a_j$  (Eq. (1)) and consequently by the chemical potentials  $\mu_k$  that are functions of the actual state of the mixture.

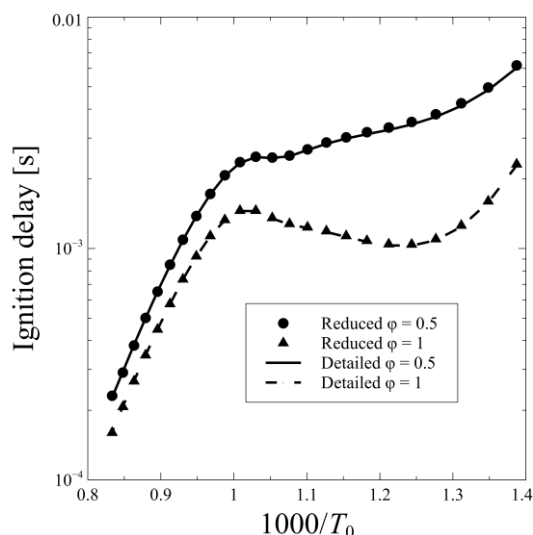


Fig. 1 Ignition delay time with the detailed and reduced mechanisms at  $P = 20 \text{ atm}$ .

## Results

To illustrate the potentiality of the approach, the proposed method was applied to obtain a reduced mechanism to compute n-dodecane ignition delay times (IDT) for a wide range of conditions, in terms of initial composition, pressure and temperature, starting from the detailed reaction mechanism proposed in [4] consisting of 451 species and 17848 reactions. A database of reaction states sampled from ignition simulations in a constant pressure batch reactor has been generated adopting the selected detailed chemical mechanism with:  $650 \text{ K} \leq T_0 \leq 1000 \text{ K}$  in steps of 50 K and  $1100 \text{ K} \leq T_0 \leq 1400 \text{ K}$  in steps of 100 K; pressures equal to 1, 5, 10 and 20 atm; and equivalence ratio ( $\varphi$ ) equal to 0.5, 0.8, 1.0, 1.2 and 1.5. A total number of 631105 states were collected to evaluate the relative importance of each reaction using Eq. (4). Then, a list of the most important species was compiled by considering

all the species participating in the most important reactions. Finally, the skeletal mechanism is obtained using an in-house code based on MECHMOD [11]. The accuracy of the reduced mechanism is the result of a compromise between the number of species and the ability to reproduce the total entropy production rate. It can be controlled by fixing a threshold value  $\varepsilon$ , and selecting only the reactions with  $\mathcal{R}_j > \varepsilon$ . Considering  $\varepsilon = 0.003$ , a reduced mechanism consisting of 134 species and 2869 reactions was generated.

The ability of this reduced mechanism to reproduce the ignition delay times is illustrated in Figure 1 for  $\varphi = 0.5$  and  $\varphi = 1$  at  $P = 20$  atm. Agreement is very good also in the range of  $T_0$  where the NTC behaviour is expected.

## Conclusions

A generalized formulation for the entropy production analysis of reaction mechanisms is proposed. A simple and theoretically well-founded procedure for the reduction of detailed mechanisms to skeletal ones has been defined and validated with respect to the evaluation of the IDT. Further validations are being carried out with respect to other fundamental combustion properties, like the laminar flame speed, and to recent alternative approaches, like the DRG method [12], to assess the potentiality of the proposed method.

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