Reduction of Detailed Chemical Mechanisms by Entropy Production Analysis in the Presence of Irreversible Reactions

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1 Introduction

The chemical composition of renewable fuels can be very complex and chemical mechanisms composed by hundreds of species and several thousands of reactions can be required for an accurate prediction of their combustion behavior [1,2]. An important step for their computationally efficient use in simulations is, therefore, the possibility to obtain reduced mechanisms with an assessed range of validity.

Kooshkbaghi et al. [3, 4] proposed an easy to implement approach for mechanism reduction that is based on the contribution of the entropy generated by the elementary chemical reactions as a measure of their importance. A simple analysis of thermodynamic states during the chemical transformation of reactants to products allows for the identification of the most relevant reactions of the detailed mechanism, thus deriving skeletal mechanisms which only include the most significant reactions for a particular application. Being based on a thermodynamic law, the degree of approximation can be selected and verified. In the original formulation [3], the evaluation of the entropy generation was based on the principle of detailed balance, a property that does not hold in the case of irreversible reactions, which are extensively adopted in the development of several detailed mechanisms for complex fuels (e.g. [6]). Therefore, it is advisable to have a more general formulation which also applies in the presence of irreversible reactions. In this work, an alternative formulation is derived starting from first principles of chemical reaction thermodynamics. A formulation valid for both reversible and irreversible reactions is derived that can be adopted as the basis for the reduction of a wide set of detailed mechanisms. The new approach is then exploited to obtain a skeletal mechanism for n-dodecane starting from the detailed reaction scheme developed by the CRECK group [6], a mechanism composed mainly by irreversible reactions.

2 Thermodynamics and entropy related functions

The second law of thermodynamics postulates the existence of an extensive state function, called entropy, S, with the following properties [7]: (a) the total entropy of a system consisting of several parts, is equal

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to the sum of the entropies of each part, (b) the change in entropy dS can be split into two parts, so that denoting by dS_{ext} the flow of entropy due to interactions with the exterior, and by dS_{int} the contribution due to changes inside the system, we have:

$$dS = dS_e + dS_i \tag{1}$$

Considering the entropy as a function of internal energy U (neglecting any other contribution to the total energy), volume V and number n of moles [8], its differential can be written in the form:

$$dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{1}{T}\sum_{k=1}^{N_S} \mu_k dn_k$$
(2)

where the definition of absolute temperature, pressure and chemical potentials [10] has been used:

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,n_j}; P = -\left(\frac{\partial U}{\partial V}\right)_{S,n_j} = -T\left(\frac{\partial S}{\partial V}\right)_{U,n_j}; \mu_k = \left(\frac{\partial U}{\partial n_k}\right)_{S,V,n_{(j\neq k)}} = -T\left(\frac{\partial S}{\partial n_k}\right)_{U,V,n_{(j\neq k)}}$$
(3)

When chemical reactions occur, the change of mole number n_k of the k-th species $dn_k = dn_{ext,k} + dn_{int,k}$ depends upon $dn_{ext,k}$, the external (due to exchange with the surrounding), and $dn_{int,k}$, the internal (due to chemical reactions) differential change [8]. Finally, for a homogeneous (closed as well as open) system, considering Eq. (1) and substituting Eq. (3) into (2), we obtain:

$$dS_{ext} = \frac{1}{T}dU + \frac{P}{T}dV - \frac{1}{T}\sum_{k=1}^{N_S} \mu_k dn_{ext,k}$$
$$dS_{int} = -\frac{1}{T}\sum_{k=1}^{N_S} \mu_k dn_{int,k}$$
(4)

where dS_{int} represents the entropy change due to chemical reactions. 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]:

$$\frac{dn_{int,k}}{dt} = V \sum_{j=1}^{N_R} (\nu_{kj}^P - \nu_{kj}^R) (q_j^f - q_j^r)$$
(5)

where ν_{kj}^P and ν_{kj}^R are the stoichiometric coefficients on the product and reactant sides 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. Substituting Eq. (5) in Eq. (4)), we obtain the rate of change of entropy due to chemical reactions:

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

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The quantity:

$$a_j = -\sum_{k=1}^{N_S} \mu_k (\nu_{kj}^P - \nu_{kj}^R)$$
(6)

is the chemical affinity (or De Donders affinity) of the j-th reaction [8]. Finally, the relative contribution of each reaction to the total (internal) entropy production is defined as

$$r_{j} = \frac{dS_{int,j}/dt}{dS_{int}/dt} = \frac{a_{j}(q_{j}^{f} - q_{j}^{r})}{\sum_{i=1}^{N_{R}} a_{j}(q_{i}^{f} - q_{i}^{r})}$$
(7)

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

$$r_{j} = \frac{\ln(q_{j}^{f}/q_{j}^{r})(q_{j}^{f} - q_{j}^{r})}{\sum_{j=1}^{N_{R}} \ln(q_{j}^{f}/q_{j}^{r})(q_{j}^{f} - q_{j}^{r})}$$
(8)

Some remarks are needed by comparing Eq. (7) with Eq. (8), the latter adopted in the original formulation of [4]. It is explicitly observed that the validity of the principle of detailed balance implies the positivity of entropy production for each reaction in the scheme (each reaction describes a separate process that realizes only the corresponding transformation, and at equilibrium each elementary process is equilibrated by its reverse process). However, reaction mechanisms are often constructed adopting many reactions that violate the principle of detailed balance. This is indeed the case when there are several reactions defined as irreversible, 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 [5]). Therefore, the general expression of Eq. (7) is preferable even if for some reactions negative values of r_j can arise. This is not in contrast with modern thermodynamics, indeed, if there are two different processes/reactions taking place simultaneously in the same system, it is possible to have [9]:

$$d_i S_1 < 0$$
 $d_i S_2 > 0$ & $d_i S = d_i S_1 + d_i S_2 \ge 0$

3 Entropy analysis

We are interested in 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 given by the expression:

$$\mathcal{R}_{j} = \frac{|a_{j}(q_{j}^{f} - q_{j}^{r})|}{\sum_{j=1}^{N_{R}} |a_{j}(q_{j}^{f} - q_{j}^{r})|}$$
(9)

In Eq. (9) an important role is played by the chemical affinity a_j (Eq. (6)) and consequently by the chemical potentials μ_k . For a mixture of ideal gases [10]

$$\mu_k(T, P) = \mu_k^{pure}(T, P) + RT\ln(X_k)$$

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where μ_k^{pure} is the chemical potential of the pure species and X_k its molar fraction. For a simple singlecomponent system, the chemical potential is equal to the specific Gibbs free energy [10]:

$$\mu_k^{pure}(T, P) = g_k(T, P) = g_k(T, P^0) + RT \ln(P/P_0)$$

where P^0 is the standard state pressure (usually 1 atm). Finally, the standard state specific Gibbs free energy $g_k(T, P^0)$ can be evaluated from standard state enthalpies and entropies

$$g_k(T, P^0) = RT(h_k^0)/(RT) - (s_k^0)/R$$

Standard state enthalpy and entropy can be computed from thermodynamic data by adopting the NASA polynomials [11].

4 Results

The proposed approach was applied for the construction of a skeletal mechanism for n-dodecane that was used in the computation of ignition delay times (IDT) starting from the detailed reaction mechanism proposed by CRECK Modeling Group at Politecnico di Milano [7] consisting of 451 species and 17848 reactions. Figure 1 illustrates the time instants used to define the relevant states where the contribution to entropy production by chemical reaction were computed. A database of ignition time simulations, as the one illustrated in Fig. 1, in a constant pressure batch reactor was generated adopting the selected detailed reaction mechanism in the ranges of initial temperatures $650 \text{K} \leq T_0 \leq 1000 \text{K}$ with $\Delta = 50 \text{ K}$ steps and $1100 \text{K} \leq T_0 \leq 1400 \text{K}$ with $\Delta = 100 \text{ K}$ for pressures equal to 1, 5, 10 and 20 atm, and equivalence ratio equal to $\varphi = 0.5, 0.8, 1.0, 1.2$ and 1.5.



Figure 1: Temporal evolution of temperature computed during autoignition of n-dodecane in a constant pressure batch reactor using the detailed mechanism ($\varphi = 1$; p = 1 atm, $T_0 = 650$ K). (a), (b) and (c) are the states collected for the analysis.

A total of 631,105 states were used to evaluate the relative importance of each reaction following the application of Eq. (9) and establish the most important reactions to keep in the skeletal mechanism. Using a tool developed with including some routines of pyMARS [13], the detailed scheme is processed to retain only the important reactions and construct the skeletal mechanism. This is done by selecting only the reactions with \mathcal{R}_n greater than a fixed threshold value ε . The accuracy of the reduced scheme is a compromise between the number of species and the ability to reproduce the same total entropy production rate as shown in Fig. 2. A threshold $\varepsilon = 0.003$ has been selected as a compromise between accuracy and number of species



Figure 2: Number of species of the skeletal mechanism versus the threshold parameter ε .

of the reduced mechanism. This choice has led to generate a reduced mechanism with 134 species and 2869 reactions showing an error below the 5% in the NTC and low temperature regions, while the error increases by diminishing the temperature up to a maximum 23% at the highest temperature and lowest pressure.



Figure 3: IDT with the detailed and reduced mechanisms at P = 1 atm (left) and P = 20 atm (right).

The ability of this reduced mechanism to reproduce the ignition delay times is illustrated in Figure 3 for $\varphi = 0.5, 1.0$ and 1.5 and P = 1 and 20 atm. The agreement is very good also in the range of T_0 exhibiting negative temperature dependence behavior.

5 Conclusions

A generalized formulation for the entropy production analysis of reaction mechanisms is proposed for mechanism reduction and validated with respect to the ignition delay time of n-dodecane. A compact skeletal

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mechanism was obtained, with a number of species and reactions that compare to those obtained with recent alternative approaches, like the DRG method [14].

Further validations are carried out with respect to other fundamental combustion properties like the laminar flame speed, to determine if these mechanisms can produce reliable results in more general combustion configurations.

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