GENERALIZED ENTROPY PRODUCTION ANALYSIS FOR MECHANISM REDUCTION

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Abstract
This paper introduces a generalized formulation for the entropy production analysis. The use of relations valid under the hypothesis of validity of the principle of detailed balance, that is violated in the remarkable case of irreversible reactions, is avoided by using more general expressions for the entropy generation due to the chemical reactions. As a result, the new formulation is applicable to generate reduced mechanisms involving both irreversible reactions or ad hoc estimated reverse rates.

Introduction

The need to introduce fuels derived from renewable sources to reduce their carbon footprint is driving several efforts to improve the investigation of chemical mechanisms. Indeed, very often the composition of such fuels is more complex and very complex mechanisms are required for a proper assessment of their combustion behavior [1,2]. An important step is therefore the possibility to obtain reduced mechanisms with assessed range of validity.

Recently, a new approach was proposed by Kooshkbaghi et al. [3,4] for mechanism reduction, that is based on the analysis of the entropy generated by the elementary chemical reactions. This approach allows to identify with a simple analysis of thermodynamic states during the chemical transformation of reactants to products, the most relevant steps of the detailed mechanism, thus deriving skeletal mechanism which only including the most significant reactions for a particular application. Being based on 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. [5]). It is therefore advisable to have a more general formulation that holds even in presence of irreversible reactions. This is the aim of this work. It is shown that an (at least) equivalent formulation can be derived starting from first principles of chemical reaction thermodynamics that is fully valid for both reversible and irreversible reactions, thus leading to a

formulation that can be adopted for the reduction of detailed mechanisms.

Theoretical background

The second law of thermodynamics postulates the existence of a state function, called entropy with the following properties [6]:

- The entropy of the system 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 parts. Denoting by dS_e the flow of entropy, due to interactions with the exterior, and by dS_i 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 [7], its differential can be written in the form:

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

where the definition of absolute temperature, pressure and chemical potentials [8] has been used:

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

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 [7]:

$$dn_k = dn_{ext,k} + dn_{int,k} \tag{3}$$

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.

Finally, for an homogeneous (closed as well as open) system[1], considering the equation (1) and substituting the equation (3) into equation (2), we obtain:

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

[1] Having neglected all other forms of contribution to the total energy, inside changes of internal energy cannot arise in the homogeneous system.

$$dS_{int} = -\frac{1}{T}\sum_{k=1}^{N_S} \mu_k \, dn_{int,k} \tag{5}$$

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 [7]:

$$\frac{dn_{int,k}}{dt} = V \sum_{j=1}^{N_R} \left(\nu_{kj}^{P} - \nu_{kj}^{R}\right) \left(q_j^f - q_j^r\right) \tag{6}$$

where ν_{kj}^{P} and ν_{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. Substituting the equation (6) in equation (5), we obtain the rate of change of entropy due to chemical reactions:

$$\frac{dS_{int}}{dt} = -\frac{V}{T}\sum_{k=1}^{N_S}\sum_{j=1}^{N_R} \mu_k \left(\nu_{kj}^{P} - \nu_{kj}^{R}\right) \left(q_j^f - q_j^r\right) \tag{7}$$

Since the quantity:

$$a_j = -\sum_{k=1}^{N_S} \mu_k \left(\nu_{kj}^{P} - \nu_{kj}^{R}\right) \tag{8}$$

is the chemical affinity (or De Donder's affinity) of the *j*-th reaction [7], we can write the rate of change of entropy due to chemical reactions in the form:

$$\frac{dS_{int}}{dt} = \frac{V}{T}\sum_{j=1}^{N_R} a_j \left(q_j^f - q_j^r\right) \tag{9}$$

Finally, we define the relative contribution of each reaction to the total (internal) entropy production as:

$$r_j = \frac{\frac{dS_{int,j}}{dt}}{\frac{dS_{int}}{dt}} = \frac{a_j\left(q_j^f - q_j^r\right)}{\sum_{j=1}^{N_R} a_j\left(q_j^f - q_j^r\right)} \tag{10}$$

In the absence of deviations from the principle of detailed balance, the chemical affinity can be given in terms of production rates [6]: $a_j = RT\, ln\left(q_j^f / q_j^r\right)$. Therefore, the relative contribution of each reaction to the total (internal) entropy production can be written as:

$$r_j = \frac{\ln\left(q_j^f / q_j^r\right)\left(q_j^f - q_j^r\right)}{\sum_{j=1}^{N_R} \ln\left(q_j^f / q_j^r\right)\left(q_j^f - q_j^r\right)} \tag{11}$$

Some remarks are needed by comparing Eq. (10) with Eq. (11), the latter previously adopted in [4]. 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 (each reaction describes a separated process that realize only the corresponding transformation and at equilibrium, each elementary process is equilibrated by its reverse process). However, usually reaction mechanisms are formed adopting many reactions that 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). Therefore, adopting the general expression of Eq. (10), for some reactions negative values of r_j can arise, but the global entropy production is always positive.

Entropy analysis strategies and results

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 given by the expression:

$$\mathcal{R}_j = \frac{\left|a_j\left(q_j^f - q_j^r\right)\right|}{\sum_{j=1}^{N_R}\left|a_j\left(q_j^f - q_j^r\right)\right|} \tag{12}$$

In Eq. (12) an important role is played by the chemical affinity a_j (Eq. 8) and consequently by the chemical potentials μ_k. For a mixture of ideal gases [8]:

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

where μ_k^{pure} is the chemical potential of the pure species and X_k its molar fraction. For a simple single-constituent system, the chemical potential is equal to the specific Gibbs free energy [8]:

$$\mu_k^{pure}(T,P) = g_k(T,P) = g_k(T,P^0) + R\,T\;\; ln\left(\frac{P}{P^0}\right)$$

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:

$$g_k(T,P^0) = RT\left(\frac{h_k^0}{R\,T} - \frac{s_k^0}{R}\right)$$

Standard state enthalpy and entropy can be computed from thermodynamic data by

adopting the NASA polynomials [9].

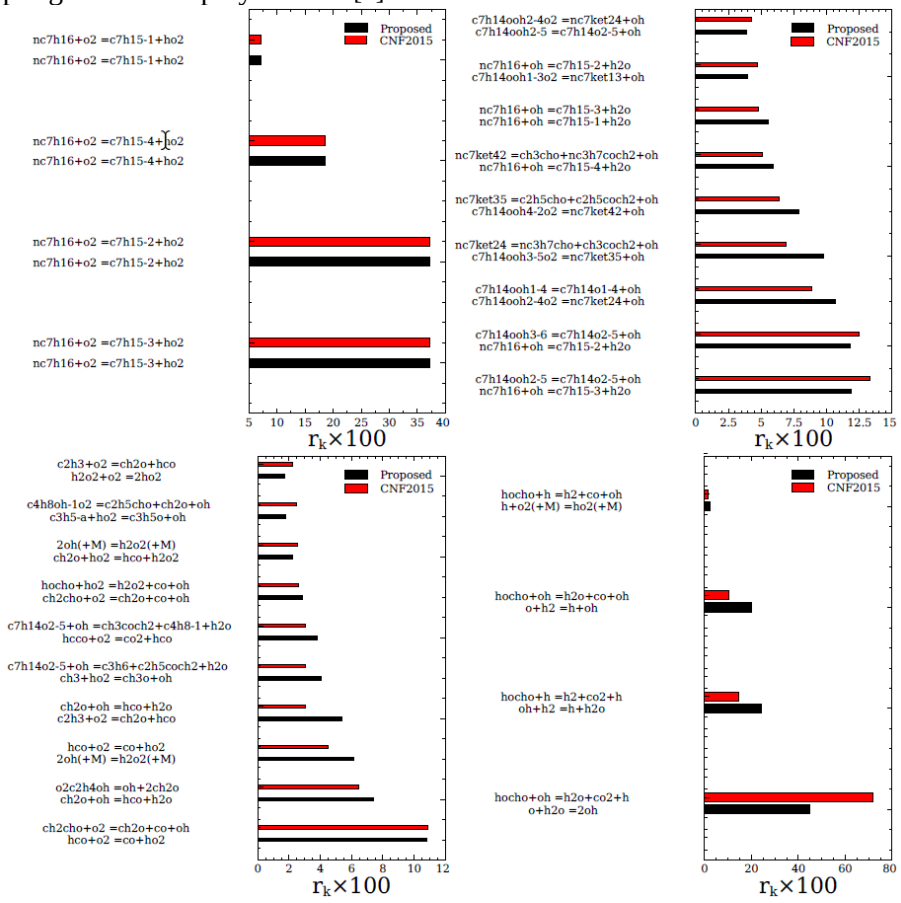

Figure 1. Selected reactions with the generalized entropy production criterion. In lexicographic order: first decomposition reactions, 0 s; heavy molecules decomposition, 0.03 s; lighter molecules reactions, 0.1 s; termination reactions, 0.16 s. Adiabatic reactor operating at P = 1 atm, ϕ = 1 and T = 650 K.

Results

The proposed analysis was applied to the study of the *n*-heptane reaction mechanism proposed in [10]. The comparison between the formulation given by Eq. (10) with respect to the formulation given by Eq. (12) is performed by studying the entropy production during the auto-ignition of a stoichiometric mixture at initial temperature 605 K and pressure 1 atm at the four different times: 0, 0.03, 0.1, 0.16 s (Figure 1). The initial decomposition reactions of *n*-heptane remain exactly the same. Differences are found during the subsequent evolution, which become more pronounced towards the final products. As revealed by the second subplot, the two criteria select different heavy molecules of the C7- groups. The new formulation gives preference to simpler molecules and to reactions forming

radical OH or the H2O final product. Similarly, the third subplot for the new formulation includes many intermediate smaller molecules, mostly in the C3- and C2- groups as well as molecules including oxygen and hydrogen atoms, while the original formulation leads to the inclusion of further C7- molecules as well as C4- and C2- molecules, thus limiting the participation of molecule not including carbon. The last subplot shows the greater differences: only reactions involving exclusively molecules formed by hydrogen and oxygen atoms are selected with the new formulation. On the basis of these results, a different reduced mechanism, adopting the same strategy for reduction as proposed in [3], is obtained.

Conclusions

A generalized formulation for the entropy production analysis of reaction mechanisms is proposed. With respect to the original formulation [3], the new one applied to the study of *n*-heptane combustion in a batch reactor select different reactions, leading to a reduced mechanism that include simpler molecules. Further analysis is required to determine the possibility to adopt these new mechanisms.

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