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Asymptotic Analysis in obtaining reduced kinetic mechanisms

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1 Introduction

Computer simulations with detailed kinetic mechanisms are more complicated due to the existence of highly reactive radicals, which induce a significant stiffness in the system of governing equations due to differences, of several orders of magnitude, in timescales of conversion between species. Consequently, there is the need to develop, from these detailed mechanisms, the corresponding reduced mechanisms with fewer variables and moderate stiffness, maintaining a good level of accuracy and comprehensiveness of the detailed kinetic mechanisms [2].

Several reduction techniques have been developed in recent years: CSP (Computational Singular Perturbation), ILDM's (Intrinsic Low Dimensional Manifolds), DRG (Directed Relation Graph), lumping, sensitivity analysis, among others. But, for the final stage of reduction the most widely used method is the steady state assumption (QSSA), which sometimes is combined with partial equilibrium (PE). These hypotheses allow the elimination of some species and the subsequent conversion of differential equations into algebraic equations.

2 Asymptotic Analysis in Mechanisms Reduction

The assumptions of QSSA and PE may be justified by making the asymptotic analysis, which is a method used to describe a limit behaviour [1]. A chemical kinetic problem can be written as a ODE's system involing the concentration vector c and the vector k, in which each component is the specific rate $k_i = AT^{\beta}e^{-Ea/RT}$ of reaction i [2, 4].

A simple example of the application of asymptotic analysis can be seen in reducing the hydrogen mechanism [3]. The skeletal mechanism has eight reactions that are shown in the Table 1. For the elementary reactions presented in the table, the balance equations can be written as

$$w_H = -w_1 + w_2 + w_3 - w_5 - w_6 - w_7, \qquad w_{HO_2} = w_5 - w_6 - w_7 - w_8, \tag{1}$$

$$w_O = w_1 - w_2 + w_4, \qquad w_{H_2} = -w_2 - w_3 + w_7, \tag{2}$$

$$w_{O_2} = -w_1 - w_5 + w_7 + w_8, \qquad w_{H_2O} = w_3 + w_4 + w_8, \tag{3}$$

$$w_{OH} = w_1 + w_2 - w_3 - 2w_4 + 2w_6 - w_8, \tag{4}$$

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where $w_{S_i} = \dfrac{dc_i}{dt}$ is the production rate of species S_i. Assuming that species O, OH and

Table 1: Hydrogen Mechanism [3]

	Reaction	A	β	E
$1f$	$H + O_2 \rightarrow O + OH$	2.0×10^{14}	0.0	16800
$1b$	$O + OH \rightarrow O_2 + H$	1.575×10^{13}	0.0	690
$2f$	$O + H_2 \rightarrow OH + H$	1.8×10^{10}	1.0	8826
$2b$	$OH + H \rightarrow O + H_2$	8.0×10^{9}	1.0	6760
$3f$	$H_2 + OH \rightarrow H_2O + H$	1.17×10^{9}	1.3	3626
$3b$	$H_2O + H \rightarrow H_2 + OH$	5.09×10^{9}	1.3	18588
$4f$	$OH + OH \rightarrow H_2O + O$	6.0×10^{8}	1.3	0
$4b$	$H_2O + O \rightarrow OH + OH$	5.9×10^{9}	1.3	17029
5	$H + O_2 + M^a \rightarrow HO_2 + M^a$	2.3×10^{18}	-0.8	0
6	$H + HO_2 \rightarrow OH + OH$	1.5×10^{14}	0.0	1004
7	$H + HO_2 \rightarrow H_2 + O_2$	2.5×10^{13}	0.0	700
8	$OH + HO_2 \rightarrow H_2O + O_2$	2.0×10^{13}	0.0	1000

HO_2 are in steady-state ($w_{S_i} = 0$), and eliminating some of the fastest consumption rates, namely w_2, w_3 and w_7 for O, OH and HO_2, respectively, one obtains balance equations, whose stoichiometry corresponds to the global mechanism of two reactions

$$(I)\ \ 3H_2 + O_2 \ \ \rightarrow \ \ 2H + 2H_2O, \ \ (II)\ \ 2H + M \ \ \rightarrow \ \ H_2 + M$$

with rates $w_I = w_1 + w_6$ and $w_{II} = w_5$.

3 Conclusions

One of the main objectives of reducing mechanisms is minimize computational time, needed in the CFD (Computational Fluid Dynamics) treatment of reactive flows. The contribution of the present work goes in this direction.

References

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