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Development of a new Automated Mechanism Generation Tool

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1. Introduction

The development of detailed reaction networks has become an integral part of modern reaction engineering because simulations done with such kinetic models help to optimize existing technical processes and to design new applications in an efficient and cost effective way. Detailed kinetic mechanisms are often large, containing thousands of reactions among hundreds of species. Manual development of those mechanisms is tedious and prone to errors. Furthermore, the maintenance of such reaction sets, e.g. to ensure completeness and consistency, is anything but straightforward. These reasons provided and still provide the motivation to develop automated mechanism generators in industry and academia, and a considerable number of such programs is nowadays available. However, most mechanism generators have limited scopes and capabilities and are therefore restricted in their application range.

For automated mechanism generating software to produce reliable predictions it has to be able to represent molecules and radicals in a unique way and to retrieve, calculate or estimate thermodynamic properties for those. In addition, the code has to be able to identify all possible reactions and to assign appropriate rate parameters to those. Finally, criteria need to be implemented to decide which species and reactions to incorporate into the kinetic model and when to terminate the generation process. In the framework of my ARAID appointment, a new automated mechanism software (TRAMGEN, Truly Rate-based Automated Mechanism GENerator) will be developed. The poster presentation will outline the concept and the status of this project.

2. Theoretical methods

Benson´s Group Additivity (GA) is a well-established method to rapidly calculate thermodynamic data of species for which reliable experimental or theoretical data is not available. This method is based on the assumption that a thermodynamic function (and some other properties) can be calculated from contributions (GAV) of all substructures (groups) a molecule is made of. Further additive terms (´non-next neighbour interactions´, NNI) are introduced to correct for non-local contributions such as steric interactions, cis- or trans- orientations or resonance effects. In this study high-level quantum mechanical methods are used to create the GAV and NNI databases needed for Benson´s method. More specifically, the CBS-QB3 level of theory is used as implemented in the Gaussian G09 and G16 suites of programs [1]. The obtained electronic energy is converted with the atomization method to the heat of formation. Statistical mechanic functions allow to calculate the entropy, heat capacities and thermal contribution to the enthalpy. Full details about the procedure can be found in a previous publication [2].

The CBS-QB3 method combined with transition state theory is used to calculate the rate coefficients of reactions. For each reaction class, rate coefficients are calculated for a series of analogous molecules and the results are generalized as “Rate Rules” or again through Group Additivity. QRRK or RRKM theory is used to investigate the pressure-dependence of reactions.

3. Results and discussion

The basic program structure of automated mechanism generating software is shown in Figure 1. The user specifies the inlet composition, pressure, temperature, reaction time and reactor type (batch or plug flow). The reactant species are used to populate the species pool. Each iteration, a single species is taken

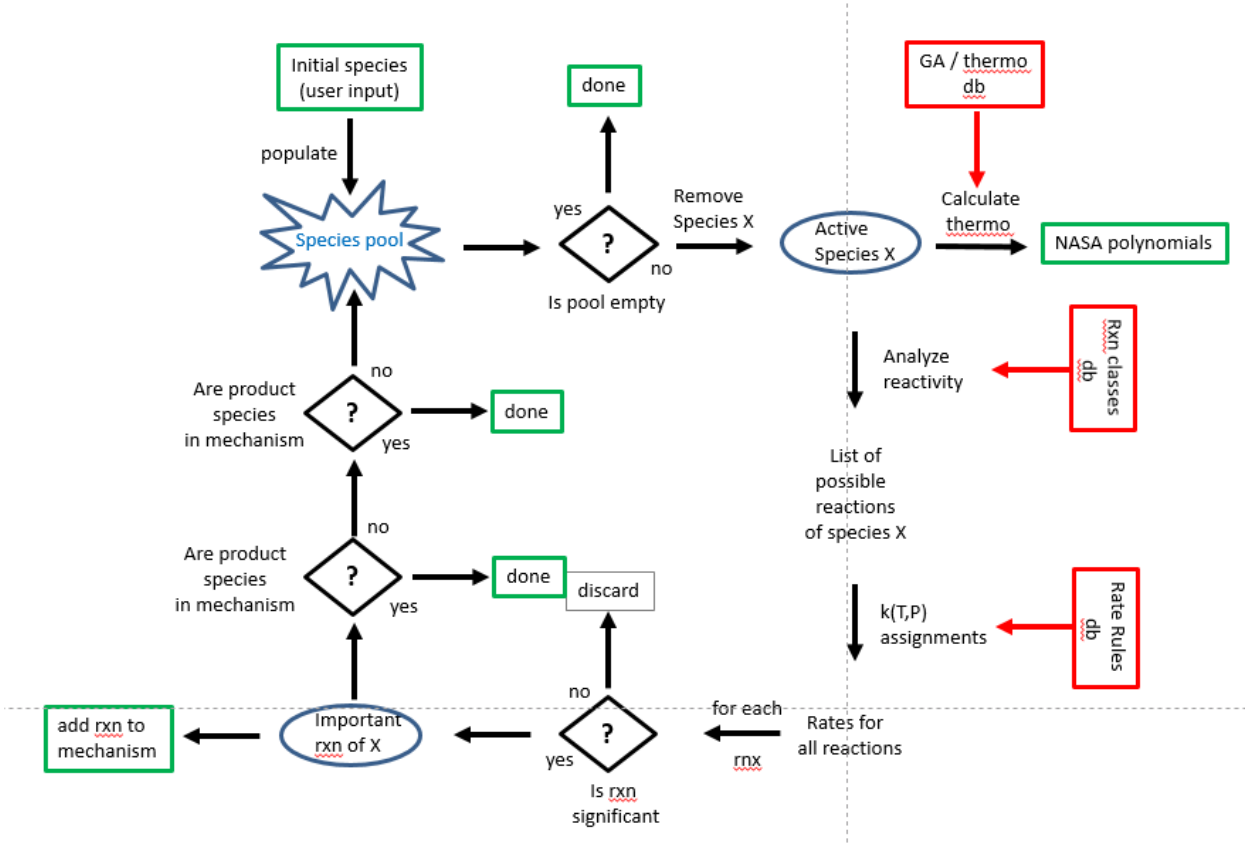

Figure 1:Conceptual flow diagram of TRAMGEN, a new automated mechanism generator.

from this pool (active species X) until the pool is empty and the program terminates. With the help of the Group Additivity database the thermodynamic properties are determined and stored as NASA coefficients. The structure of the species is analyzed and all its possible reactions are identified based on criteria stored in the Reaction Class database. Rate Rules retrieved from databases are employed to determine the reaction rates at the given temperature and pressure condition. An objection function is evaluated to determine if a given reaction is important. Unimportant reactions are ignored and the important ones are added to the kinetic mechanism. New product species are added to the species pool. This rate based algorithm ensures that the kinetic model is complete and at the same time concise.

Besides coding, the main challenge is to create the required databases. Previous work by the author and others developed Group Additivity parameters for many H/C/O containing species (see e.g. [2] and references therein) and more parameters will have to be calculated in the future. The same is true for reaction families, which have been largely identified in the past. Some Rate Rules can be found in the literature; others will be determined as part of this project with the ab initio methodology discussed earlier.

An important aspect is validation. Experiments will be carried out at the University of Zaragoza to produce accurate speciation data. Combined with data sets from the literature these will serves as stringent test to demonstrate the reliability of predictions by TRAMGEN-generated models.

4. Conclusions

A new automated mechanism generator is being developed. Compared to existing ones, it will be fully rate based, meaning that only reactions that contribute significantly to the chemistry are kept. The user will have very limited influence on the final model, making it “truly rate based and truly automatic”. The poster will present the actual status of this project.

References

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