Exercise 1: Introduction to detailed kinetic mechanisms

Computational tools

Kinetic pre-processor from the `OpenSMOKE++ Suite` [1]

Reaction mechanism

Detailed mechanism of hydrogen and carbon monoxide oxidation [2]

Purpose

Familiarize the student with the standard `CHEMKIN` format [4, 5] to write kinetic mechanisms and thermodynamic and transport properties. Make the student aware of need to pre-process thermodynamic, transport and kinetic data to check the existence of possibile inconsistencies or unphysical behaviours [3].

Background

The stoichiometry and the reaction rate of each reaction must be completely characterized, by providing all the relevant data. In addition, for each species involved in the kinetic mechanism, thermodynamic properties are needed (specific heta at constant pressure, enthalpy and entropy). Moreover, if transport phenomena are non-negligible, transport properties of species must be properly taken into account.

The `CHEMKIN` standard is today the most adopted format to write kinetic mechansisms and thermodynamic and transport properties. Thus, a first objective of this practical session is to get familiar with the most important `CHEMKIN` rules to correctly write a complete kinetic mechanism and/or to interpret existing mechanisms written in this format.

Since detailed kinetic mechanisms can easily involve hundreds of species and thousands of reactions, it is of paramount importance to havecomputational tools able to check the internal consistency of data describing the kinetic mechanism (i.e. the `CHEMKIN` files). As an example, in the following a non-exaustive list of relevant checks which should be always performed to verify a kinetic mechanism is reported:

- continuity of thermodynamic properties in the whole range of temperature
- the atomic balances for every reaction must be satisfied
- possible existence of duplicated reactions
- physical constraints on collisional integrals for the evaluation of ransport properties.

All the relevant checks can be automatically performed using a proper kinetic pre-processor, which analyzes the input files, reporting possible errors or warnings. Moreover, the pre-processor has also an additional purpose, i.e. to reorganize the data in a format which is more convenient for successive calculations.

Tasks

In this first practical session we will learn how to write kinetic mechanisms in `CHEMKIN` format and ow to pre-process them. We will use the `POLIMI_TOT_NOX_1412.CKT` thermodynamic database and the `POLIMI_TOT_NOX_1412.TRC` transport properties database. They are the databases shared by every

kinetic scheme from the CRECK Modeling Group, based on data available in the literature, NIST[1] and Burcat's[2] websites. For the third task we will use the `POLIMI_H2CO_1412.CKI` kinetic mechanism [6], describing the combustion chemistry of hydrogen and carbon monoxide (14 species and 33 reactions) .

1. Pre-process a database of thermodynamic data written in `CHEMKIN` format. Check the internal consistency of supplied data and look at possible unphysical behavior. Improve, if needed, the consistency of thermodynamic data.

2. Pre-process a database of transport properties written in `CHEMKIN` format. Analyze the main results of polynomial fitting of transport data.

3. Pre-process complete kinetic-mechanism, together with thermodynamic and transport properties. Check if reversible reactions are written properly, i.e. if the equivalent reverse kineti constants are feasible.

References

[1] A. Cuoci, A. Frassoldati, T. Faravelli, and E. Ranzi. Opensmoke++: An object-oriented framework for the numerical modeling of reactive systems with detailed kinetic mechanisms. *Computer Physics Communications*, 192:237–264, 2015. doi: 10.1016/j.cpc.2015.02.014.

[2] A. Frassoldati, T. Faravelli, and E. Ranzi. Kinetic modeling of the interactions between no and hydrocarbons at high temperature. *Combustion and Flame*, 135(1-2):97–112, 2003.

[3] R. Kee, M. Coltrin, and P. Glarborg. *Chemical Reacting Flows: Theory and Practice*. Wiley-Interscience, 2003.

[4] R.J. Kee, F. Rupley, and J.A. Miller. Chemkin ii: A fortran chemical kinetics package for the analysis of gas-phase chemical kinetics. *Sandia Report SAND89-8009 - Sandia National Laboratories*, 1989.

[5] R.J. Kee, F.M. Rupley, E. Meeks, and J.A. Miller. Chemkin-iii: A fortran chemical kinetics package for the analysis of gas phase chemical and plasma kinetics. Technical report, 1996.

[6] E. Ranzi, A. Frassoldati, R. Grana, A. Cuoci, T. Faravelli, A.P. Kelley, and C.K. Law. Hierarchical and comparative kinetic modeling of laminar flame speeds of hydrocarbon and oxygenated fuels. *Progress in Energy and Combustion Science*, 38(4):468–501, 2012.

[1] `http://webbook.nist.gov/chemistry/fluid/`
[2] `http://garfield.chem.elte.hu/Burcat/burcat.html`