Modelling experimental lack of knowledge in chemical networks: elicitation of sum-constrained variables

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The experimental measurements of a multi-pathways reaction rate is often made in two steps. In a first experiment, the reactants loss rate, called *global rate constant*, is measured, while in a different experiment, the proportion of matter going into each channel, called the *branching ratio*, is determined. Therefore two different problems have to be adressed: a pdf for the global rate constant and correlated pdfs for the branching ratios must be separately elicited. Whereas standard loguniform or lognormal elicitation are relevant for the global rate constant, branching ratios are more tricky to model and should be adapted to different experimental scenarii.

Dirichlet modelling enables one to obtain sum-constrained random variables by sampling in the simplex of any n-dimension hypercube, thus any number of branching ratios.[2] It was previously used to describe simple branching ratios problems.

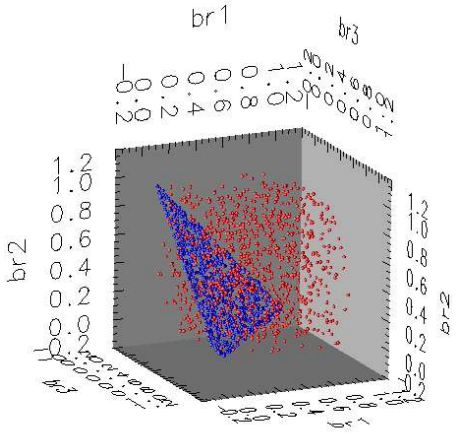

Figure 1: Latin Hypercube Sampling of (1) red: independant variables; (2) blue: sum-constrained variables sampled under a Dirichlet uniform distribution

Electron Dissociative Recombination (EDR), where free electrons recombine with positive ions to produce neutral species, adds a new difficulty for branching ratios elicitation: for heavy ions, the distribution of neutral products is incompletely characterized. In recent experiments on hydrocarbon ions, only the carbon repartition can be measured, leaving the hydrogen repartition and thus the exact neutral species identity unknown.[1]

The specifics of EDR call for a generalization of our previous work, in the form of hierarchiral Dirichlet Distributions. This approach enables us to simulate chemical networks that cannot be consistently treated by conventional "deterministic" methods.

Implementation of such probabilistic trees requires new standard data models for chemistry databases.

$$
\begin{array}{lll}
 & \text{C repartition} & \text{H repartition} \\
 & \text{(measured)} & \text{(unknown)} \\
\mathrm{C_4H_9^+ + e^-} \left\{ \right. & \longrightarrow \mathrm{C_4} & \left\{ \begin{array}{l} \rightarrow \mathrm{C_4H_2 + 3H_2 + H} \\ \vdots \\ \rightarrow \mathrm{C_4H_2 + 7H} \end{array} \right. \\
 & \longrightarrow \mathrm{C_3 + C} & \left\{ \begin{array}{l} \rightarrow \mathrm{C_3H_8 + CH} \\ \vdots \\ \rightarrow \mathrm{C_3H_3 + CH_2 + 2H_2} \end{array} \right. \\
 & \longrightarrow \mathrm{C_2 + C_2} & \left\{ \begin{array}{l} \rightarrow \mathrm{C_2H_6 + C_2H_2 + H} \\ \vdots \\ \rightarrow \mathrm{2C_2H_2 + 2H_2 + H} \end{array} \right.
\end{array}
\tag{1}
$$

References

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