Robust Mechanism Discovery with Atom Conserving Chemical Reaction Neural Networks

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Highlights

- Autonomously identify reaction mechanisms from integral reactor data
- Robust against noise, missing data, and sensor drifts – ideal for real-world data sets
- Physically sound and fully interpretable

1. Introduction

Rational reactor design requires a reliable mechanistic understanding of the reaction kinetics. In this regard, machine learning has emerged as a valuable tool that automates mechanism discovery, reduction, and numerical acceleration [1]. The performance of neural networks for these applications is significantly improved by implementing *a priori* physical knowledge in the model's structure [2, 3]. In this work we focus on implementing the atom balance in neural networks. Previously, this has either been done explicitly through a soft constraint in the loss function, or a post-processing step, or indirectly by embedding the stoichiometric matrix into the model's structure. However, in the case of mechanism discovery and reduction, the stoichiometric matrix is generally unknown and subject to optimization. We propose a dedicated element balance layer (shown green in Fig. 1) for neural networks models of chemical kinetics that enforces atom conservation as a hard constraint without requiring the stoichiometric matrix. We implement this layer into the chemical reaction neural network (CRNN) recently developed by Ji and Deng [4] and demonstrate that enforcing the atom conservation greatly increases the model's ability to identify physically sound reaction mechanisms from low quality data [5].

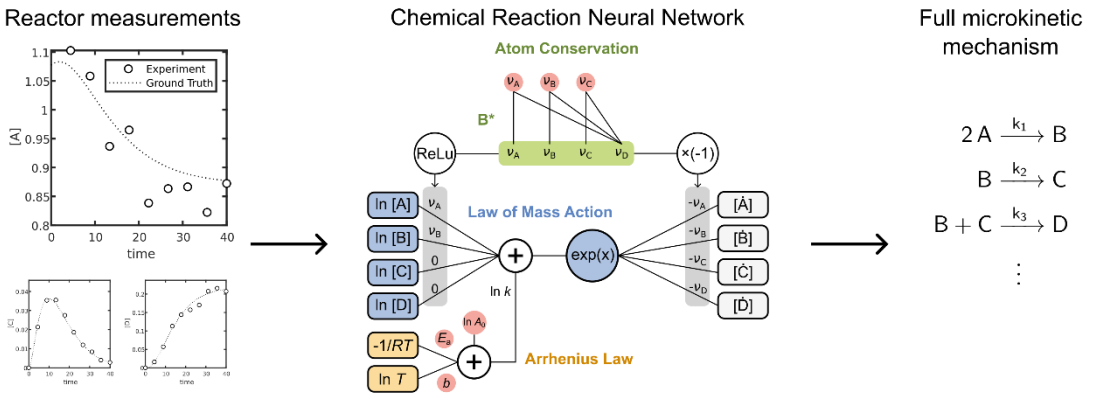

Figure 1. The mechanism discovery workflow uses concentration measurements from an integral reactor to train the atom conserving chemical reaction neural network (trainable parameters are highlighted in red). It encodes the law of mass action, the Arrhenius law and in contrast to the standard CRNN also the atom conservation. The trained model is directly equivalent to a classic microkinetic mechanism and is easily implemented in reactor simulations.

2. Methods

The CRNN is a digital twin of the classic chemical reaction network that encodes the Arrhenius equation and the mass-action law in a neural network. To learn from concentration data, it is trained in the context of a neural ODE, i.e. wrapped with an ODE solver. The resulting CRNN concentration profiles are compared to the provided concentration data. We use the Julia language implementation of CRNN available at github.com/DENG-MIT/CRNN. It uses the differential programming package *DifferentialEquations.jl* to enable backpropagation of gradients through the ODE solver. The mean absolute error loss of the normalized concentrations is used and minimized using the ADAM optimizer

to adjust the CRNN parameters. The parameters B* of the newly proposed atom conservation layer are determined in a preprocessing step as the reduced column echelon form basis of the molecular matrix null space, i.e. computed within a single line of MATLAB code.

3. Results and discussion

Embedding the atom balance into neural networks facilitates mechanism discovery. One of our test cases is biodiesel production where embedding the atom balance increases the model's robustness against noise and offsets in the training data. Concentration data are obtained by integrating the transesterification kinetics of palm oil derived palmitin glycerides (TG, DG, and MG) with methanol as described by Darnoko and Cheryan [6] for 20 different initial compositions. To emulate real experimental data, we add 5% gaussian noise and in the case of reactant TG an offset of 0.2 to simulate a faulty sensor calibration.

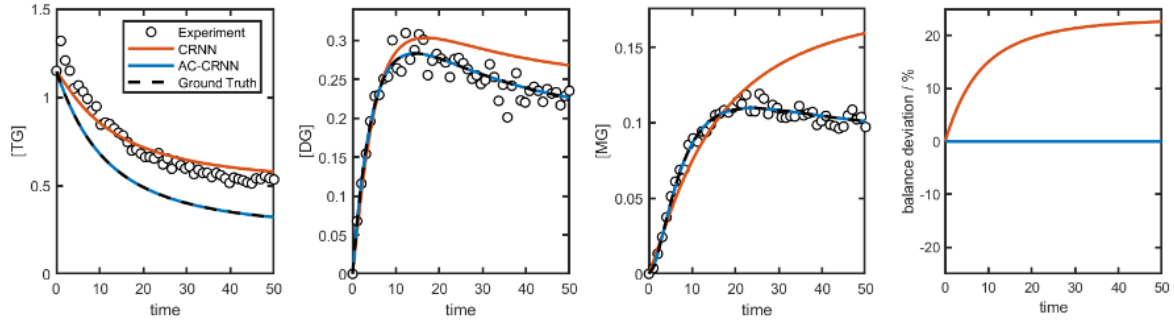

Figure 2. Biodiesel production concentration profiles obtained from mechanism discovery by standard CRNN (red) and atom conserving CRNN (AC-CRNN, blue) using synthetic measurements from 20 integral reactor experiments (symbols).

As the standard CRNN model adapts to the erroneously high concentrations of the reactant TG, an excessive amount of the other glycerides DG and MG is formed. This leads to an error in the atom balance by more than 20%. The newly proposed atom conserving CRNN (AC-CRNN) is stable towards the sensor offset (Fig. 2) and recovers the correct underlying mechanism with a perfectly closed atom balance. Additionally, it has 40% fewer parameters to optimize, resulting in faster training times.

4. Conclusions

Chemical reaction neural networks have established as the most advanced tool for autonomous mechanism discovery and are used in many fields, especially (bio-)chemical engineering [4,7]. While they encode the law of mass action as well as the Arrhenius law, mass- and atom conservation are still violated. We enforce the fundamental law of atom conservation by adding a dedicated neural network layer which can be interpreted as constraining stoichiometric coefficients to physically realizable combinations. The resulting atom conserving chemical reaction neural networks improve training stability and speed, offer robustness against noisy and missing data, and require less data overall. As a result, we anticipate increased model reliability and greater utilization of the potential of real-world data sets, which will assist chemical reaction engineers. Finally, our proposed element conservation layer is compatible with any feed forward neural network that predicts kinetics and should therefore be useful also for surrogate modeling and mechanism reduction.

References

[1] J. A. Bennett, M. Abolhasani, *Curr. Opin. Chem. Eng.* **2022**, *36*, 100831.
[2] F. A. Döppel, M. Votsmeier, *Chem. Eng. Sci.* **2022**, *262*, 117964.
[3] F. A. Döppel, M. Votsmeier, *React. Chem. Eng.* **2023**, *8*, 2620–2631.
[4] W. Ji, S. Deng, *J. Phys. Chem. A* **2021**, *125*, 1082–1092.
[5] F. A. Döppel, M. Votsmeier, *ChemRxiv Preprint* **2023**, DOI: 10.26434/chemrxiv-2023-1r389
[6] D. Darnoko, M. Cheryan, *J. Am. Oil Chem. Soc.* **2000**, *77*, 1263–1267.
[7] E. Nieves, R. Dandekar, C. Rackauckas, *BioRxiv Preprint* **2023,** DOI: 10.1101/2023.09.11.557164

Keywords
Atom conservation; Kinetic model; Mechanism discovery; Physics enhanced machine learning