

# Optimizing a Molecular Model for CO<sub>2</sub> by Fitting Its Parameters to Large Experimental Datasets

Sebastian Hielscher<sup>C, S</sup> and Monika Thol

*Lehrstuhl für Thermodynamik, Ruhr-Universität Bochum, Bochum, Germany*

*S.Hielscher@thermo.ruhr-uni-bochum.de*

Gábor Rutkai, Andreas Köster and Jadran Vrabec

*Lehrstuhl für Thermodynamik und Energietechnik, Universität Paderborn, Paderborn, Germany*

Roland Span

*Lehrstuhl für Thermodynamik, Ruhr-Universität Bochum, Bochum, Germany*

Due to increased computer performance, recent progress in molecular models (force fields) and its simulation methods, simulated thermodynamic data have already been used to extend experimental data sets to develop fundamental equations of state (FEOS) [1-2]. However, the accuracy of the simulated thermodynamic properties is limited by the quality of the underlying molecular model. The common standard of optimizing molecular models nowadays only considers vapor-liquid equilibrium data ( $p_v$ ,  $p'$ ,  $h_{vap}$ ). The presented optimized potential model (PM) for CO<sub>2</sub> is based on the rigid model published by Merker et al. [3]. New potential parameters were optimized to thermodynamic properties in the homogenous fluid region as well as to vapor-liquid-equilibrium (VLE) data. CO<sub>2</sub> was considered because its fluid region is described by the highly accurate reference FEOS of Span and Wagner [4]. The experimental data available for CO<sub>2</sub> are generally reproduced by this FEOS within their experimental uncertainty. Therefore, the FEOS was used to generate the property data required to optimize the PM. The iterative optimization procedure uses parameter variations of the original model. When a parameter of a PM is varied by a small magnitude, a shift in the thermophysical properties from the parameter variation can be observed. By changing all parameters of the model, one at a time, a system of equations can be set up to solve the minimization problem. After the optimization, the accuracy of the PM was significantly improved for saturated liquid density and vapor pressure. In the homogenous region, the accuracy of the isochoric heat capacity and speed of sound was improved. The representation of other thermodynamic properties remained nearly unchanged. Finally, the limitations of the optimization method were investigated. It was shown that simultaneous optimization of the PM using homogeneous and VLE data is difficult, which may be due to simplified nature of the PM.

## References

- [1] M. Thol, G. Rutkai, A. Köster, M. Kortmann, R. Span, J. Vrabec, *Chem. Eng. Sci.*, 121(6), 87-99, 2015.
- [2] G. Rutkai, M. Thol, R. Lustig, R. Span, *J. Chem. Phys.*, 139, 041102, 2013.
- [3] T. Merker, C. Engin, J. Vrabec, H. Hasse, *J. Chem. Phys.*, 132, 234512, 2010.
- [4] R. Span, W. Wagner, *J. Phys. Chem. Ref. Data*, 25(6), 1509-1596, 1996.