A Generalized Fundamental van der Waals Equation of State

Sergio E. Quiñones-Cisneros [C, S] and Stefan Pollak
Geo Process Engineering., Ruhr-University Bochum, Bochum, NRW, Germany
seqc@fvt.ruhr-uni-bochum.de

Ulrich K. Deiters
Institute of Physical Chemistry, University of Cologne, Cologne, NRW, Germany

It is now almost one and a half-century that the van der Waals equation of state (vdW EoS) was first published. The vdW EoS was the first model to describe the liquid-vapor phase transition, unifying both states at a critical point.

Another important 19th-century development was the Dieterici EoS, which was the first model to introduce an exponential term to improve the fluid's critical-compressibility performance effectively. The characteristic slow-convergence of an exponential term can make, around a critical point, the long-range fluctuations competitive with the short-range ones, resulting in a flattening of the critical isotherm and an improved critical-compressibility prediction.

The vdW EoS and the Dieterici EoS can be considered the base for today's EoS of wide industrial application. While the vdW EoS represents the origin of all cubic EoS, the Dieterici EoS, the first model incorporating an exponential term, can be considered the precursor of the Benedict–Webb–Rubin EoS and the subsequent highly accurate multiparametric empirical reference EoS.

Naturally, the extension of a two-parameters cubic EoS to mixtures is more straightforward than a multiparametric model. In the case of mixture multiparametric EoS, the current state of the art is the GERG 2008 EoS, a complex model currently limited to natural gas' main compounds.

A mathematical transformation aimed to reduce different types of EoS to a generalized van der Waals EoS form is presented in this work. The approach applies to all rational EoS, including Helmholtz reference EoS, so that a method such as the one-fluid mixing rules used for cubic EoS becomes applicable in general. Despite the simplicity of the approach, the *pvT* results are comparable to those obtained with the GERG 2008 EoS. In the first instance, using the one-fluid vdW mixing rule, the approach can be extended to a wide range of non-polar fluid mixtures.