IAPWS Certified Research Need – ICRN

Thermodynamic Properties of Humid Gases and CO_2-Rich Mixtures

Closing Statement

In 2011, the IAPWS Working Groups "Thermophysical Properties of Water and Steam" and “Industrial Requirements and Solutions” issued ICRN 27, titled “Thermodynamic Properties of Humid Gases and CO_2-Rich Mixtures”. ICRN 27 was based on the observation that severe deficiencies existed with regard to the description of CO_2-rich mixtures as they are needed for accurate system design of power plants, particularly for power plants being part of a carbon capture and storage (CCS) or utilization (CCU) process chain.

In 2011, the available information was considered not sufficiently accurate and comprehensive to permit:

(a) the evaluation of the performance of power plants with CCS now under construction or soon to be constructed;

(b) the optimization of the economic performance of these power plant systems including downstream systems for CO_2 drying, purification, compression, transport and storage, and the proper sizing of components;

(c) the development and optimization of second-generation power-generation technologies with CCS, including precise comparisons between different technical solutions.

By now, this situation has substantially improved, at least for those parts of the process chain where accurate thermodynamic property data are considered particularly relevant under technical, economic, regulatory, or safety aspects. In part triggered by ICRN 27, systematic improvements of the data situation and available thermodynamic property models have been addressed in a number of completed and partly still ongoing research projects. These projects include, for example:

The EU project IMPACTS, which supported experimental and theoretical work on mixtures of CO_2 with the main impurities to be expected for CCS processes. As a result of IMPACTS and the preceding E.ON Research Award funded Project EOS-CG, the property model EOS-CG describing mixtures of CO_2, H_2O, N_2, Ar, O_2, and CO was published.[1] The development of

[1] J. Gernert and R. Span: EOS–CG: A Helmholtz energy mixture model for humid gases and CCS mixtures. *J. Chem. Thermodyn.* **93**, 274-293 (2016).

EOS-CG was supported by experimental work carried out at Ruhr University in Germany, SINTEF in Norway, and Tsinghua University in China.

In parallel to IMPACTS, the EU project CO2QUEST addressed thermophysical property issues as well. The focus of CO2QUEST was on less accurate, but more predictive models and on the description of properties of mixtures relevant for geological CO_2 storage.

The Norwegian project BIGCCS led by SINTEF in Trondheim addressed further components relevant particularly for compression, processing and transport of captured CO_2. This work is continued in the follow-up project NCCS, also funded by the Norwegian Research Council. By now, BIGCCS and NCCS resulted in an accurate multiparameter mixture model describing a broader matrix of components; see Figure 1.

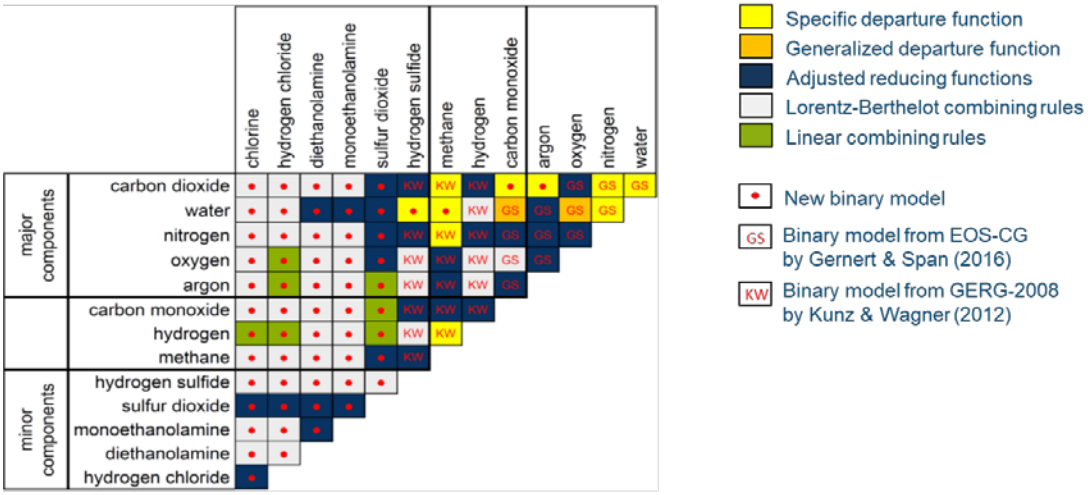

Figure 1: Components described by accurate empirical multiparameter models for CO_2-rich mixtures.[2]

At the U.S. National Institute of Standards and Technology (NIST), the dew point of water in compressed CO_2, an important parameter for pipeline transport, was measured up to 5 MPa at temperatures from 10 °C to 80 °C with smaller uncertainties than previous studies.[3] This work was partly funded by the U.S. Department of Energy. The same project produced improved correlations for the viscosity[4] and thermal conductivity[5] of pure CO_2. A related project to replace the reference thermodynamic equation of state for CO_2 is in the early stages.

[2] S. Herrig, I. Bell, T. Neumann, and R. Span, EOS-CG-2018: An Extended Fundamental Equation of State for the Thermodynamic Properties of Mixtures Relevant for CCS-Applications. International Symposium on Thermophysical Properties, Boulder, 2018.
[3] C.W. Meyer and A. H. Harvey, Dew-Point Measurements for Water in Compressed Carbon Dioxide. *AIChE J.* **61**, 2913-2925 (2015).
[4] A. Laesecke and C.D. Muzny, Reference Correlation for the Viscosity of Carbon Dioxide, *J. Phys. Chem. Ref. Data* **46**, 013107 (2017).
[5] M.L. Huber, E.A. Sykioti, M.J. Assael, and R.A. Perkins, Reference Correlation of the Thermal Conductivity of Carbon Dioxide from the Triple Point to 1100 K and up to 200 MPa, *J. Phys. Chem. Ref. Data* **45**, 013102 (2016).

Involving several groups mostly in Europe and NIST in the USA, the work on CO_2-rich mixtures relevant for CCS continues. In NCCS, future work focuses on improvements of the experimental basis and modeling of reacting systems, in order to better describe mixtures relevant for CO_2 capture.

The European ACT-program funded project ELEGANCY includes experimental work further improving the database and addressing mixtures relevant for geological storage. In the framework of ELEGANCY, an attempt is made to extend the applicability of accurate multiparameter mixture models to systems containing electrolytes and to describe mixtures consisting of natural gas and hydrogen. ELEGANCY involves groups at Imperial College in Great Britain, SINTEF in Norway, and Ruhr University in Germany.

The German project DYNAFLEX addresses accurate property models for CO_2-rich mixtures with high hydrogen content, which are considered relevant for a number of CCU concepts. DYNAFLEX also supports both experimental and theoretical work; the property related work is carried out at Ruhr University in Germany.

An overview on the status of property research for CCS and CCU was given by Span and Trusler[6] at the 17th International Conference on the Properties of Water and Steam in Prague.

Besides fluid phases, phase equilibria with dry ice and CO_2-hydrates are relevant for CCS and CCU. Phase equilibria with dry ice had already been addressed by Imperial College in Great Britain and Ruhr University in Germany when ICRN 27 was formulated. The description of hydrate formation consistent with accurate multiparameter models for fluid phases was systematically addressed over the last years by research groups at Ruhr University and TU Dresden in Germany, and at the Academy of Science in Prague. The status of this work was reported by Hielscher et al.[7] at the 17th International Conference on the Properties of Water and Steam.

Based on the broad scientific interest in thermophysical properties relevant for CCS and CCU and on the multitude of ongoing projects in this area, the IAPWS Working Groups "Thermophysical Properties of Water and Steam" and “Industrial Requirements and Solutions” consider most of the goals of ICRN 27 achieved and let ICRN 27 expire.

Prague, September 2018

[6] R. Span and J.P.M. Trusler, Capture, Transport and Storage of Carbon Dioxide – Thermodynamic Property Models for Different Tasks in an Integrated Chain of Processes. 17th International Conference on the Properties of Water and Steam, Prague, 2018.

[7] S. Hielscher, A. Jäger, V. Vinš, C. Breitkopf, J. Hrubý, and R. Span, A new model for mixed hydrates consistent with multiparameter equations of state. 17th International Conference on the Properties of Water and Steam, Prague, 2018.