Attachment 9

IAPWS Collaborative Grant Proposal

An experimental study of thermal conductivity of the binary ammonia + water system at high temperatures and pressures

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Visiting Young Scientist
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This proposal will have four principal outcomes: it will strengthen collaborations between the Department of Theoretical Bases of Thermal Engineering of the Kazan State Technological University (KSTU) and the National Institute of Standards and Technology (NIST) in the US; it will enable a young scientist to travel from the KSTU to NIST for training in best practices for calibrations, measurements and data evaluation; it will provide the IAPWS community with new measurements of thermal conductivity measurements for the aqueous system ammonia + water in wide ranges of temperature and pressure; and, it will initiate a broad program of measurements and models for the ammonia + water system.

An IAPWS Certified Research Need [1] indicated a need for properties for ammonia + water mixtures at temperatures to 866 K (593 °C) at pressures up to 35 MPa, covering the complete range of composition. In spite of research activity from 1997 to 2002 that was reported in the Closure Statement for this ICRN, thermal conductivity data are still very limited for ammonia + water mixtures.

The primary reasons for the scarcity of data are experimental difficulties related to the fact that this system is corrosive, toxic, potentially flammable, and has a high relative volatility. Special materials, safety procedures, special equipment and knowledge of their proper use are all required. Only a handful of labs, including NIST, have been able to make sufficient investment in training and materials to make such measurements.

The H2O + NH3 mixture is receiving increased attention due to the potential use of the system as a working fluid in refrigeration and power plant cycles. The binary H2O + NH3 mixture has a large technical significance in the fields of absorption refrigeration machines, absorption heat pumps, and heat transformers. To decrease environmental impact, natural working fluids such as ammonia and water have been considered as alternative refrigerants to replace chlorofluorocarbons (CFC) in some refrigeration applications. The ammonia-water mixture does not affect the atmospheric ozone layer nor does it contribute to the greenhouse effect. Therefore, the significance of this mixture in refrigeration technology is strongly increasing. Refrigeration cycles with H2O + NH3 mixtures as working fluids have been shown to reach higher coefficients of performance than traditional working fluids. Thermophysical modeling of technological processes requires information on the transport properties (viscosity and thermal conductivity) of H2O + NH3 mixtures. The important properties of viscosity and thermal conductivity are required for absorption cycle analysis and in the design of heat exchangers. Power cycles with H2O + NH3 mixtures as working fluids also have been shown to reach higher thermal efficiencies than the traditional steam turbine (Rankine) cycle with water as the working fluid. The best H2O + NH3 cycle produced approximately 40-70 % more power than a single-pressure steam cycle and 20-25 % more power than a dual-pressure steam cycle. In calculating the performance of the power cycles, accurate transport properties data of the H2O + NH3 mixture play an important role. The demand to decrease the consumption of primary energy leads to optimization of technological processes. To improve the H2O + NH3 cycle efficiency and to operate apparatus at high temperatures and pressures, the need for pertinent data in regions beyond those covered by the available data becomes more urgent. For this aim, engineering design of absorption air-conditioning equipment utilizing the H2O + NH3 cycle requires accurate transport property data of H2O + NH3 mixtures over a wide range of T, P, x. However, the existing reported transport property data cover a limited range of T, P, x, and contain large uncertainties and inconsistencies. A number of speeches about geothermal power cycle applications have been presented at the latest geothermal conference in Germany, 2010. At NIST, two groups from the Thermophysical Properties Division, TRC (M. Frenkel) and Theory and Modeling of Fluids Group (E. Lemmon), have received repeated requests from various industrial companies for transport properties of the ammonia + water mixture.

Accurate thermal conductivity data are also essential to the development of a reference correlation equation. The currently available thermal conductivity data [2-4] cover only very limited temperature, pressure, and concentration ranges. Most reported data are at atmospheric pressure and at temperatures up to 375 K. Moreover, the data reported by Baranov et al. [4] are presented graphically (the data were never published). The other two publications [2,3] are very old (1898 and 1937). A detailed analysis of the reported data is presented in Ref. [5]. Both the Thermophysical Properties Division of NIST (Dr. R. Perkins) and KSTU (Prof. Tarzimanov's team, Vargaftik's student) have extensive experience and capabilities in accurate thermal conductivity measurements covering wide ranges of temperature, pressure, and concentration and their modeling (Dr. M. Huber). In a previous IAPWS project we have reported [6-8] PVTx and CvVTx data for the aqueous system (H2O + ammonia) in the near-critical and supercritical regions. For the reasons mentioned earlier, the labs of TSTU and NIST are among the few research facilities in the world with capabilities for H2O + ammonia thermal conductivity measurements at high temperatures and high pressures.

Using other funding, Prof. Tarzimanov's team in the KSTU Labs will investigate thermal conductivity in a temperature range from 298 to 363 K and at pressures up to 20 MPa for the concentrations 25, 50, and 75 mass % of ammonia, with an uncertainty in thermal conductivity of less than 2 %. This investigation will provide reliable thermal conductivity data by using a hot wire technique [9-11].

Following the experiments, we plan to bring a younger KSTU Labs scientist to the Boulder Labs of NIST for 6 months. Ph.D. Student Fanis Shamsetdinov will be our top choice, since his PhD dissertation is on thermophysical properties of aqueous systems. Mr. F. Shamsetdinov will assist Dr. Huber and her team in the Boulder Labs with the following tasks: (1) analysis of the thermal conductivity data for water+ammonia mixture; and, (2) comparison with published measurements and models; (3) develop new thermal conductivity model for the mixture; (4) prepare MS of the paper for publication. As an additional educational component of his visit, we will conduct detailed discussions and comparisons of the experimental thermal conductivity techniques used in the KSTU Labs with those used in the Boulder Labs, methods for precise gravimetric mixture preparation, a propagation of uncertainties analysis, round-robin measurement comparisons, and establishing a chain of traceability to national and international standards.

Budget

We propose a total budget of $18,000 for this. This would pay for the travel expenses and 6-month visit for Mr. Fanis Shamsetdinov or other young KSTU scientist for his work in Boulder with the US-based research team. A project report will be prepared and submitted to IAPWS by the next annual meeting.

Leveraging of the IAPWS Support

The research team has planned a comprehensive research project on the ammonia + water system, involving partnerships with university-based researchers. To leverage the support from IAPWS, we will seek additional support from other agencies. Toward the end of the proposed IAPWS project, one or more proposals will be prepared to support the following tasks: (1) additional measurements of transport properties (viscosity data for the ammonia + water system and thermal diffusivity measurements at high temperatures and high pressures); (2) development of new models for thermal conductivity and viscosity.

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Proposal of the Young Scientist IAPWS Project for 2011

Development of Thermodynamic Models for Hydrates in Water–Carbon Dioxide Mixture

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Introduction and Background

Water-carbon dioxide mixtures play an important role both in nature (environmental and geological processes) and in many industrial applications (natural gas industry, energy production, etc.). The H_2O–CO_2 system is a binary mixture with rather complex phase equilibria including a total of six phases. The phase diagrams of the mixture water-carbon dioxide were discussed for example by Wendland [1], Diamond [2], and Longhi [3]. Phase equilibria of the H_2O–CO_2 system show liquid-liquid immiscibility over a large range of *p*-*T* conditions, interrupted critical curves, and formation of crystalline water-based solids – hydrates [4]. The proposed project will focus especially on the last mentioned phenomenon occurring in the H_2O–CO_2 system.

The CO_2-hydrate, clathrate, is the only intermediate solid compound in the water-carbon dioxide system, since the end-member solid phases, water ice and solid CO_2, do not admit mutual solution. Clathrate has a nominal composition of $CO_2 \cdot 7.5H_2O$, although this composition can slightly vary with temperature and pressure in reality. CO_2-clatharte-hydrate occurs already at relatively high temperatures. For instance, the first quadruple point, when four phases (vapor + aqueous liquid + water ice + clathrate) are in equilibrium, has *p*-*T* coordinates of 1.0 MPa and –1.5°C. As a consequence, the CO_2-hydrates can result for example in pipeline blockage during natural gas transportation. Accurate knowledge of clathrate in the water-carbon dioxide mixture is therefore of great interest particularly for the petroleum industry.

As already noted, the mixture water-carbon dioxide is a rather complex non-ideal system that should be further investigated. The inviting working group (Lehrstuhl für Thermodynamik in Bochum) has recently made some progress in describing the role of carbon dioxide in aqueous solutions. Jäger and Span [5, 6] developed a fundamental equation for solid CO_2 – dry ice. The fluid phase equilibrium of the H_2O–CO_2 system is being modeled by a modified GERG [7] equation of state now. Span and Gernert [8] have verified that the GERG-2004 equation of state accurately describes the H_2O–CO_2 system after some refitting to relevant experimental data.

At the current stage, the intermediate solid phase of the H_2O–CO_2 system, i.e. clathrate, needs to be treated. Clathrate plays an important role in the behavior of the water-carbon dioxide mixture. However, it has been described only partially. It is therefore planned to develop a fundamental equation for CO_2-hydrates under the cooperation of Lehrstuhl für Thermodynamik in Bochum and the Institute of Thermomechanics in Prague.

Scope of the project

In the proposed project, possibilities of an accurate modeling of thermophysical properties of clathrate in H_2O–CO_2 system will be studied. The project can be split into two parts.

- An overview regarding the available data for CO_2-hydrates is already prepared. In the preliminary part of the project, a detailed literature review will be done to complete the data set.
- The main aim of the project is to develop a fundamental equation describing the clathrate phase in H_2O–CO_2 systems. Similarly as the equation of state for dry ice [5, 6], the equation for CO_2-hydrates will be explicit in Gibbs energy $g = g(T, p)$. The Gibbs energy will in principle be determined by fitting the data for isobaric heat capacity and molar volume $v(T, p)$. The new equation of state for clathrate should also fulfill equilibrium conditions with other phases, especially with water ice described by the

IAPWS equation of state [9] and with dry ice modeled with the equation by Jäger and Span [5, 6].

Purpose of the Project and Justification for IAPWS Support

The purpose of the collaborative project with IAPWS is to analyze available experimental data for the clathrate phase of the H_2O–CO_2 system and to develop a fundamental equation of state for CO_2-hydrate. The IAPWS funding will make it possible to spend six months at Ruhr-Universität in Bochum in a single stay starting in February 2011.

The proposed project is closely connected with the research activities of both concerned departments; namely with investigation of water mixtures, metastable water, CO_2 separation, and nucleation in natural gas. Results from the project would therefore be further used at both departments and will contribute to different IAPWS activities in a broader sense.

Budget estimate (in EURO)

Subsistence for 6 months: IAPWS Young Scientist Grant … **12.000 €**

Travel (round trip) and insurance will be covered by the Institute of Thermomechanics.

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Main publishing activities

- G. Hallewell, V. Vacek, V. Vinš: Properties of saturated fluorocarbons: Experimental data and modeling using perturbed-chain-SAFT, *Fluid Phase Equilibria* 292 (1-2), 2010, pp. 64-70
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