EXPIRED

IAPWS Certified Research Need - ICRN 6

Thermophysical Properties of Ammonia-Water Mixtures

The IAPWS Working Group - Thermophysical Properties of Water and Steam has examined the published work in the area of the thermodynamic and transport properties of ammonia-water mixtures required for accurate system design of power plants and has found that the existing information is deficient in a number of respects.

The available information is not sufficiently accurate and comprehensive to permit:

(a) the evaluation of the performance of power plants now under construction and soon to be constructed,

(b) the optimization of the economic performance of power plant systems and the proper economic sizing of components, and

(c) the design, operation, and calibration of control systems used to monitor and control power plants which use ammonia/water mixtures as their working fluids.

Although encouraging this work, IAPWS is not able under its statutes to provide financial support. The IAPWS contact can provide any further development information and will liaise between research groups.

Issued by the

International Association for the Properties of Water and Steam

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Thermophysical Properties of Ammonia/Water Mixtures

Background:

For over a century, power plants have been in service utilizing water as their working fluid. In recent years, accurate formulations of the thermophysical properties of steam (enthalpy, entropy, density, temperature, pressure, thermal conductivity, viscosity) have been developed with international cooperation through IAPWS. These formulations and the steam tables derived from them are used in the design and testing of turbines, boilers, condensers, heat exchangers, pumps, and other equipment. These steam properties are also used by system designers to specify the performance of the components which make up a modern power plant. The properties are also required by the owner at the time the power plant is accepted to check the performance guarantees and to monitor the performance of the system over time, particularly for degradations in efficiency.

Validated thermophysical properties are also required for calculations concerning the safety of power plants. Various control equipment is designed to shut power plants down when operating parameters exceed the specified criteria. These conditions are determined on the basis of measurements which, in turn, are interpreted with the aid of the steam tables.

Steam turbine power plants costing as much as a billion dollars are bought and sold with guaranteed performance quoted to within 0.25%. In many cases, performance is warranted with the possibility of substantial liquidated damages being paid for failure to meet warranties. Whether the seller is liable for these damages depends upon measurements which, in turn, are again interpreted with the aid of steam properties.

Recent developments indicate that improved thermodynamic performance can be obtained from power plants if the present working fluid, water, is replaced by a mixture of ammonia and water. The mixtures used cover the entire range of compositions, from 0 to 100% ammonia. The cycle is described in "Development of the Adjustable Proportion Fluid Mixture Cycle" by C.H. Marston (Mechanical Engineering, Vol. 114, No. 9, Sept. 1992, p. 76-81). The best known such cycle is the Kalina Cycle.

In addition to their importance in potential power plant applications, accurate properties data for ammonia/water mixtures are also important for use in the design and operation of absorption refrigeration systems.

1. The Range of Thermodynamic Properties Required

The applications of ammonia-water mixtures in power plant design include very high temperature systems, as occur in the use of coal in "direct fired" power plants (866 K) to more modest temperatures, such as those in nuclear reactors (644 K), and relatively low temperatures in geothermal and industrial waste heat systems (373-473 K). The pressures used may vary from feed pump delivery pressures of 34.5 MPa down to condenser pressures of 0.002 MPa.

For every combination of pressure, temperature, and mass fraction of ammonia, it is necessary to have values of the specific enthalpy, entropy, and density.

Because of the importance of boiling and condensation phenomena in these cycles, it is also essential to have good information on the surface tension of ammonia-water mixtures.

2. The Range of Transport Properties Required

The proper design of turbines and pumps together with the design of heat exchangers requires in addition to the thermodynamic properties, good knowledge of the viscosity and thermal conductivity of ammonia-water mixtures over the complete range of temperatures and pressures cited for thermodynamic properties.

3. Stability of Ammonia-Water Mixtures

The constituents of ammonia-water mixtures will decompose significantly at high temperatures. The effect of different construction materials as catalysts has not been established.

Ammonia decomposition is heterogeneous, that is, it is enhanced by contact with a heated surface and occurs near the walls of a flow stream. It is desirable to operate the equipment at as high a temperature as possible. Therefore, there is a need to characterize the catalytic nature of different materials which may be of interest in high temperature plant components (superheaters, for example).

4. Previous Work and Current Studies

An important bibliography of experimental work on the ammonia-water system was published in 1986 by the U.S. National Bureau of Standards (predecessor to the National Institute of Standards and Technology - NIST): **NBS Special Publication 718 -- Bibliographies of Industrial Interest: Thermodynamic Measurements on the Systems CO_2-H_2O, $CuCl_2$-H_2O, H_2SO_4-H_2O, NH_3-H_2O, H_2S-H_2O, $ZnCl_2$-H_2O, and H_3PO_4-H_2O**, by B.R. Staples *et al.* This report and an experimental study by Gillespie *et al* (AIChE symposium Series, 256; Vol. 83, 1987: **Vapor-Liquid Equilibrium Measurements on the Ammonia-Water System from 313 K to 589 K**) were sponsored by the Design Institute for

Physical Property Data of the American Institute of Chemical Engineers. The 1964 report of the U.S. Institute of Gas Technology (Research Bulletin No. 34; **Physical and Thermodynamic Properties of Ammonia-Water Mixtures**, by Marcriss *et al.*) presents tabulated thermophysical properties for the water-rich system up to about 500 K and for the ammonia-rich fluid up to 390 K.

Among the more recent studies, the article by Smolen *et al.* (**Vapor Liquid Equilibrium Data for the NH_3-H_2O System and Its Description with a Modified Cubic Equation of State**, J. Chem. Eng. Data 36; 202, 1991) can be cited. In this paper, as well as many others, an attempt to describe the system with a simple (i.e. cubic) thermodynamic surface is made. It is noted throughout the literature there is a concentration on VLE data (to the near exclusion of single-phase properties). Finally, it is also noted that even the VLE data exhibit large inconsistencies when comparing the results of different studies.

Current work is underway at NIST to begin the development of standard reference thermophysical properties for the ammonia-water system for geothermal applications. It is necessary that any mixture of thermodynamic surface must reduce to a water formulation such as that of IAPS 84 and to an ammonia surface for instance (Haar and Gallagher, **Thermodynamic Properties of Ammonia**, J. Phys. Chem. Ref. Data 7; 635, 1978) for the pure components. The theoretical models being examined include scaled equations in the region of the critical locus for VLE calculations and extended corresponding states algorithms to calculate mixture properties. The work at NIST includes a limited measurement program to resolve the major discrepancies in the experimental VLE database and to supply selected data over limited ranges where none are currently available. These new data will have a major impact on the development of standard reference models for applications in the range of geothermal power cycles. Additional funding, as well as collaboration with other domestic and international groups, will be required to achieve a definitive study of the ammonia-water system. The NIST program does not currently address the questions concerning surface tension or the stability and catalysis issues which are also extremely important.

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