EXPIRED

ICRN-10

IAPWS Certified Research Need - ICRN 10

pH Measurements and Potentiometric Studies of Supercritical Aqueous Solutions

The IAPWS Working Group - Physical Chemistry of Aqueous Solutions has examined the published work in the area of pH measurements and potentiometric studies of supercritical aqueous solutions.

IAPWS recognizes that there is a requirement for work to be pursued in this field and has prepared this document to assist potential investigators obtain sponsorship. Specifically, development of new experimental techniques is needed. Theoretical and experimental studies are required to develop high temperature and pressure pH standard solutions over a wide range of temperature up to 400°C.

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

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pH Measurements and Potentiometric Studies of Supercritical Aqueous Solutions

The Problem

High quality pH measurements and potentiometric studies are amongst the most powerful tools that are available for exploring the thermodynamics, kinetics and other physical-chemical processes that occur in high temperature aqueous solutions. This approach has already been intensively applied for measuring pH in aqueous solutions (Macdonald et al., 1992), as well as for studying acid-base equilibria (Mesmer et al., 1988) at temperatures up to 300 °C. While some preliminary pH measurements have been already made in supercritical aqueous systems (Macdonald et al., 1992), no quantitative potentiometric and pH measurements have yet been carried out in supercritical aqueous environments.

Needed Research Activities

Research in this field is proceeding on two fronts; namely, (1) the application of conventional cells to conditions and environments found in the power plant industry, and (2) the application of electrochemical cells (flowing and static) to laboratory-scale, high precision research.

In the former application, recent advances in the development of several types of membrane, metal/metal oxide pH sensors (Kriksunov and Macdonald, 1995), as well as improvements in understanding the behavior of reliable external pressure balanced reference electrodes (Lvov et al., 1995, 1996) offer an opportunity for research on the problem of potentiometric studies and pH measurements of supercritical aqueous solutions at temperatures as high as 500 °C. In this case, the needed research activities should involve the development of both high temperature (supercritical conditions) ion-selective and reference electrodes. Both hydrogen electrodes and membrane pH sensors have to be investigated as possible ion-selective electrodes for these studies. Both internal silver/silver chloride and external pressure-balanced electrodes may be considered as possible reference electrodes in supercritical high temperature aqueous environments.

Hydrogen electrode concentration cells have been used routinely in the laboratory to give unique, accurate information on equilibrium thermodynamics involving such processes as hydrolysis and complexation (Mesmer et al., 1988). However, in the main, these investigations have involved static cells with an upper working limit of 300 °C, due to the presence of Teflon and the inherent existence of two phases within the cell. The presence of hydrogen has also limited the choice of solutes to those with compatible reduction potentials. Future designs under consideration with supercritical capabilities must involve a single liquid phase, flow-through design. These pH measurements must be carried out accurately. Errors in pH should be less than 0.05. Moreover, the hydrogen electrodes could probably be replaced in a second design variation with yttria-stabilized zirconia electrodes.

A significant part of the research should be focused on the problem of standardizing of the high-temperature pH measurements and development of high temperature "pH standards" which have not been defined yet at temperatures higher than 150 °C.

Expected Results

The development of accurate potentiometric and pH measurements at temperatures higher than 300 °C will greatly improve our understanding of corrosion and oxidation processes in supercritical aqueous solutions and lead to the creation of highly sensitive pH monitoring of power plant cycles working at supercritical conditions. In addition, high quality studies of acid-base and redox equilibria will be available leading to the derivation of both standard thermodynamic properties and activity coefficients of aqueous solution components.

References

1. L.B. Kriksunov, D.D. Macdonald, Advances in Measuring Chemistry Parameters in High Temperature Aqueous Systems. in: Physical Chemistry of Aqueous Systems: Meeting the Needs of Industry, Eds. H.J. White, J.V. Sengers, D.B. Neumann and J.C. Bellows. Begell House Publishers. NY 1995, pp 432-440.

2. S.N. Lvov, G. Perboni, M. Broglia, High Temperature pH Measurements in Dilute Aqueous Ammonia Solutions. in: Physical Chemistry of Aqueous Systems: Meeting the Needs of Industry, Eds. H.J. White, J.V. Sengers, D.B. Neumann and J.C. Bellows. Begell House Publishers. NY 1995, pp 441-448.

3. S.N. Lvov and D.D. Macdonald. Estimation of the Thermal Liquid Junction Potential of an External Pressure Balanced Reference Electrode. J. Electroanalytical Chem. 1996, 403, p. 25-30.

4. D. D. Macdonald, S. Hettiarachchi, H. Song, K. Makela, R. Emerson, and M. Haim, Measurements of pH in Subcritical and Supercritical Aqueous Systems, *J. Solut. Chem.* 1992, 21, p. 849-881.

5. R.E. Mesmer, W.L. Marshall, D.A. Palmer, J.M. Simonson, H.F. Holmes. Thermodynamics of Aqueous Association and Ionization Reactions at High Temperatures and Pressures. *J. Solut. Chem.* 17, 1988, p. 699-717.

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