

## Closure Document

of the ICRN (10)

### **pH Measurements and Potentiometric Studies of Supercritical Aqueous Solutions.**

Issued: May 1996. Extended to July 2005. IAPWS Contact: S. Lvov.

Considering that the S. Lvov is not longer active in IAPWS, and the subject is covered in the paper:

*S.N. Lvov H. Gao, D.D. Macdonald, Advanced flow-through external pressure-balanced reference electrode for potentiometric and pH studies in high temperature aqueous solutions, [Journal of Electroanalytical Chemistry Volume 443, Issue 2](#), 20 February 1998, Pages 186-194*

the Working Group on Physical Chemistry of Water and Steam (Item 13 from the Minutes 2011) recommended a closing statement

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## Results Achieved

### **Abstract:**

A new flow-through external pressure-balanced reference electrode (FTEPBRE) has been developed for potentiometric and pH measurements in high temperature aqueous solutions. The unique feature of this advanced FTEPBRE is that the reference solution flows through the electrode so that the concentration of solution across the thermal liquid junction is well defined. Because the electrolyte concentration profile in the reference electrode is maintained constant, uncertainty in the thermal liquid junction potential (TLJP) can be eliminated at a given temperature and pressure. We have employed the silver-silver chloride |platinum|hydrogen non-isothermal electrochemical system for potentiometric measurements of potentials between HCl (aq) solutions of 0.01 and 0.001 mol kg<sup>-1</sup> at temperatures up to 633 K and at pressures of 275 and 338 bar. The results of the measurements have been compared with calculations made using the available thermodynamic data, and good agreement, within  $\pm 3$  to 10 mV, between the calculated and the measured potentials is obtained. We concluded that the advanced reference electrode can be used to make accurate potentiometric measurements (within a few mV) in aqueous systems over wide ranges of temperatures and pressures. Also we demonstrated an ability of the thermocell to measure pH with high accuracy of  $\pm 0.04$  to 0.09 over wide ranges of temperature and pressure.