Electrochemical Studies of the Thermodynamic Properties of Aqueous Solutions at Temperatures above 300 °C

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The particular features of high temperature aqueous solutions have been widely recognized and employed in many areas of science and technology. However, due to the difficulty of performing experimental measurements at high temperature and pressure, there is a great scarcity of electrochemical studies under high temperature subcritical and supercritical conditions. The electrochemical studies of high temperature aqueous solutions carried out by the author and his research group at Penn State University will be presented in this paper. Particularly, high temperature potentiometry of aqueous solutions using a new flow-through electrochemical system [1] will be discussed in detail. The electrochemical system allows the accurate potentiometric measurements above 300ºC. The main system components include a flow-through external Ag/AgCl reference electrode, a flow-through Pt(H2) indicator electrode, and a flow-through YSZ(Hg/HgO) indicator electrode. The purity and concentration of the solutions are maintained by relatively rapid flow. The achieved precision of the potentiometric measurements, using the flow-through electrochemical cell, is found to be ±5 mV or less. As an example employing the system described above, the association constants of HCl(aq) at temperatures from 300 to 400ºC were recently obtained. Also, using both the Pt(H2) and YSZ(Hg/HgO) electrodes, the Henry's constant of H2(aq) was measured at temperatures between 300 and 450ºC. Therefore, it was found that reliable potentiometric data can be obtained using a flow-through electrochemical cell at temperatures up to 450ºC and densities down to about 0.1 g/cm^3.

[1] S.N. Lvov, G.C. Ulmer, X.Y. Zhou, H.L. Barnes, D.D. Macdonald, S.M. Ulyanov, L.G. Benning, D.E. Grandstaff, M. Manna, and E. Vicenzi, Progress on Electrochemistry and Structure of Yttria-Stabilized Zirconia Sensors for Hydrothermal pH Measurements, Chemical Geology, 2003 (in press).