There is a disagreement in the values of the standard state thermodynamic properties for ionization of water calculated from potentiometric [1] and calorimetric measurements [2] at temperatures above 473 K. Accurate standard state (infinite dilution) thermodynamic properties for the ionization of water at high temperatures and pressures are very important in the study of almost all ionic equilibria in aqueous solutions. Because of increasing non-ideality of the electrolytes in even dilute solutions [3], the extrapolated experimental thermodynamic values to standard state (infinite dilution) conditions become more uncertain as the temperature increases. Since ionization of water is perhaps the most important acid-base reaction, it was decided to reinvestigate this disagreement between potentiometric and calorimetric measurements. Using ionic additivity, values for the changes in the standard state Gibbs free energy, enthalpy, entropy, heat capacity, and molar volume for ionization of water, at steam saturated pressure up to the temperature of 573.15 K, are calculated from the recently available corresponding values for the standard state partial molar properties of HCl(aq) [4], NaCl(aq) [5], and NaOH(aq) [6, 7]. Comparison of the present study with the literature data indicate that in fact there are no disagreements between the above mentioned standard state thermodynamic properties for ionization of water calculated from potentiometric and calorimetric measurements. The apparent disagreement is, however, the result of the model chosen to represent the potentiometric data.

References: