

## Calculation Of Thermal Liquid Junction Potential Of Water-filled Ag/AgCl Electrode

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Pressure-balanced external Ag/AgCl electrode has been extensively used for both Pressurized Water Reactor and Boiling Water Reactor environment. Pure water is often employed as the electrode filling solution in order to prolong the lifetime. Characterization of the potential of the water-filled Ag/AgCl electrode was performed by estimating thermal liquid junction potential (TLJP) originating from thermal diffusion of ionic species in the filling solution.

The potential of thermoelectrochemical cell, Ag/AgCl/Cl<sup>-</sup>(T<sub>0</sub>),Cl<sup>-</sup>(T)/SHE(T) was analyzed and expressed as,

$$\text{Ag/AgCl vs SHE(T)} = [\Delta\phi_{\text{Ag/AgCl/Cl}^- \text{ vs SHE(T}_0)}] - \text{TLJP} + [\text{SHE(T}_0) \text{ vs SHE(T)}]$$

The first term and the third term in above equation, can be calculated by utilizing thermodynamic data available.

TLJP can be calculated by utilizing following equation.<sup>1</sup>

$$-F\nabla\phi_{\text{TLJP}} = \sum_k \frac{t_k}{z_k} \left[ (\nabla\mu_k)_{T,p} + \frac{Q_k^*}{T} \nabla T \right]$$

In above equation, Q<sub>k</sub><sup>\*</sup> means heat of transport of species k and the other symbols have their usual meanings.

This equation was analyzed and applied to water-filled Ag/AgCl electrode.

$$\begin{aligned} \text{TLJP} = & -\frac{1}{F} \int_{T_0}^T \frac{t_{\text{Ag}^+}}{z_{\text{Ag}^+}} \left[ RT \frac{d \ln \gamma_{\text{Ag}^+}}{dT} - \frac{Q_{\text{AgCl}}^*}{vT} + \frac{Q_{\text{Ag}^+}^*}{T} \right] \\ & + \frac{t_{\text{Cl}^-}}{z_{\text{Cl}^-}} \left[ RT \frac{d \ln \gamma_{\text{Cl}^-}}{dT} - \frac{Q_{\text{AgCl}}^*}{vT} + \frac{Q_{\text{Cl}^-}^*}{T} \right] \\ & + \frac{t_{\text{H}^+}}{z_{\text{H}^+}} \left[ RT \frac{d \ln \gamma_{\text{H}^+}}{dT} + \frac{RT}{m_{\text{H}^+}} \frac{dm_{\text{H}^+}}{dT} + \frac{Q_{\text{H}^+}^*}{T} \right] \\ & + \frac{t_{\text{OH}^-}}{z_{\text{OH}^-}} \left[ RT \frac{d \ln \gamma_{\text{OH}^-}}{dT} + \frac{RT}{m_{\text{OH}^-}} \frac{dm_{\text{OH}^-}}{dT} + \frac{Q_{\text{OH}^-}^*}{T} \right] dT \end{aligned}$$

The heat of transport of species k was calculated based on the Agar et al's hydrodynamic theory<sup>2</sup> and after some calculations, can be summarized as,

$$Q_k^* = -5.3174 \times 10^{11} \frac{\eta \lambda_i^0}{\epsilon_r^2} \frac{\partial \epsilon_r}{\partial T} T \quad [J / mol]$$

where, ε<sub>r</sub>, η is relative dielectric constant and viscosity of water. The values of limiting equivalent ionic conductance, λ<sub>k</sub><sup>0</sup> were adopted from Quist et al's paper.<sup>3</sup>

Concentration profile of H<sup>+</sup>, OH<sup>-</sup> was determined from the dissociation equilibrium at the very temperature where they exist, whereas that of Ag<sup>+</sup>, Cl<sup>-</sup> was calculated from the following equation.

$$m(T) = m(T_0) \exp \left( \int_{T_0}^T -\frac{Q_{\text{AgCl}}^*}{2RT^2} dT \right)$$

As a boundary condition, solubility equilibrium of AgCl at room temperature was used.

The behavior of activity coefficient with temperature was calculated based on the Debye-Huckel theory.<sup>4</sup> In the end, estimated TLJP was included in the calculation of the potential of Ag/AgCl electrode and the results are

shown in Figure 2 with experimental results of our laboratory. As shown in the Figure 2, theoretical calculation quite well predicts the experimental data. Polynomial fitting results in following equation.

$$\text{Ag / AgCl vs SHE(T)} = -2.0434 + 0.030158T - 0.00011877T^2 + 1.8752 \times 10^{-7}T^3 - 1.06 \times 10^{-10}T^4$$

Therefore we conclude that our TLJP analysis for Soret steady state is valid, which is the first calculation of TLJP of water-filled Ag/AgCl electrode at steady state for high temperature application.

## References

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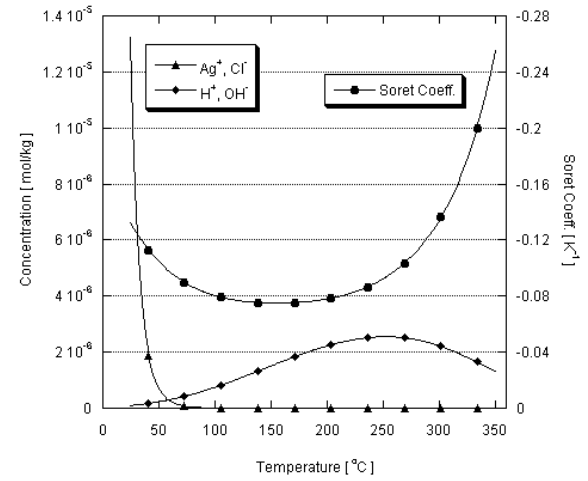


Fig.1. Concentration profiles formed by thermal diffusion of ionic species and Soret coefficient of AgCl with temperature

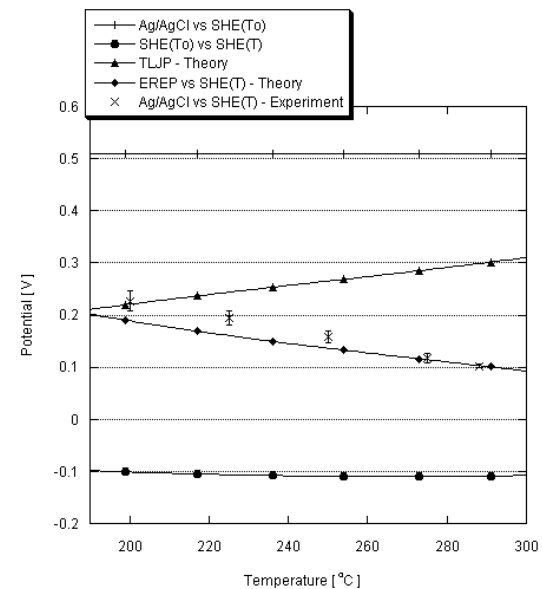


Fig. 2. Comparison of theoretically calculated potential of Ag/AgCl electrode with experimental data