

pH measurements in supercritical hydrothermal systems

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A major barrier for studying many different geologically-significant physicochemical processes in hydrothermal environment is the lack of a reliable and generally applicable method for measuring pH. If pH could be measured accurately at temperatures above 300°C, we would significantly increase our knowledge of protolitic phenomena, including the acid-base dissociation, hydrolysis, ion-pairing, solubility processes, and their associated thermodynamic properties. The development of accurate potentiometric and pH measurement techniques would yield information that will greatly improve our understanding of the thermodynamic, kinetic and surface processes in different water-rock interactions.

We have developed a flow-through electrochemical cell (FTEC) and demonstrated that it successfully operates in both subcritical and supercritical aqueous environments at temperatures up to 400°C. The FTEC consists of a previously developed flow-through external (Ag|AgCl) pressure-balanced reference electrode (FTEPBRE) (Lvov *et al.*, 1998a,b) and a modified flow-through platinum hydrogen electrode (FTPHE). The design of the FTEPBRE was similar to one described by Lvov *et al.* (1998a, Fig. 1). The stainless steel tube contained an inner tube which was constructed using a shrinkable PTFE tube in the low temperature section and a ZrO₂ tube in the high temperature section. An Ag|AgCl element and a PEEK plastic inlet tube were placed into the shrinkable PTFE tube. The reference (0.1 m NaCl) solution from the PEEK tube first flows through the PTFE tube and then through the ZrO₂ ceramic tube. A similar design was used for the FTPHE (1998a, Fig. 2). If compared to the previous design of the Pt|H₂ electrode, there were several modifications as follows: (1) the high temperature tip of the electrode was coiled and platinized; half of the length (50 cm)

of the Pt wire was used to make this tightly coiled part, whose dimensions were 1.5 cm in length and 1.5 mm in diameter; (2) the rest of the Pt wire was first covered with a ZrO₂ film which was electrophoretically deposited from a ZrO₂ sols (1.3% Yttrium, 18% ZrO₂, ALFA AESAR) and then was covered with a shrinkable PTFE in the low temperature section and with a thin Al₂O₃ ceramic tube in the high temperature section. By these means, the influence of the low temperature section of the Pt wire to the measured potential was eliminated; (3) the distance from the tip of the Pt coil to the hot end of the ZrO₂ tube was about 1 cm, and this distance was estimated based on the hydrodynamic calculations. Note that the tubing and housing of our pumps are made from plastics, while the pump pistons are made from glass. All of the other tubes in the low temperature regions in our system were PEEK plastic tubes. Therefore, in our modified experimental system, the contamination of the solution pathways from the reservoir to the hot ends of the ZrO₂ tubes was significantly minimized.

We have also carried out a detailed irreversible thermodynamic analysis of the FTEC and estimated different significant contributions to the measured potentials. The thermocell of interest is the silver-silver chloride/platinum-hydrogen, non-isothermal electrochemical system (at bottom of page), where $E^{(1)}$ is the electromotive force (e.m.f.), ϕ_L and ϕ_R are the electrostatic potentials of the left and right terminals, respectively, at ambient temperature T_1 , and T_2 is an elevated temperature that is higher than T_1 . If the reference solution is constantly renewed using the flow-through technique, the $E^{(1)}$ value is the initial e.m.f. (Lvov and Macdonald, 1997), which can be expressed on the basis of linear irreversible thermodynamics as:

$$\begin{array}{c}
 | < \text{---} T_1 \text{---} > | < \text{---} T_2 \text{---} > | < \text{---} t_1 \text{---} \\
 \text{Cu} | \text{Ag} | \text{AgCl} | 0.1\text{m NaCl(aq)} || 0.1\text{m NaCl(aq)} + m \text{HCl(aq)} | \text{H}_2(\text{Pt}) | \text{Pt} \dots \text{Pt} | \text{Cu} \quad (I) \\
 \phi_L \qquad \qquad \Delta\phi_{TD} \quad \Delta\phi_{STR(L)} \quad \Delta\phi_D \qquad \Delta\phi_{STR(R)} \qquad \qquad \Delta\phi_{TE} \quad \phi_R \\
 | \text{---} \text{---} \text{---} E^{(1)} = \phi_R - \phi_L \text{---} \text{---} \text{---} |
 \end{array}$$

$$E^{(1)} = \frac{1}{F} [\mu_{H^+}(T_2) + \mu_{Cl^-}(T_1) - \frac{1}{2}\mu_{H_2}(T_2) - \mu_{AgCl}(T_1) + \mu_{Ag}(T_1)] \quad (1)$$

$$+ \Delta\phi_{TE} + \Delta\phi_D + \Delta\phi_{STR(R)} + \Delta\phi_{STR(L)} + \Delta\phi_{TD}$$

where $\mu_{H^+}(T_2)$ and $\mu_{H_2}(T_2)$ are the chemical potentials of $H^+(aq)$ and $H_2(aq)$, respectively, in the high temperature region; $\mu_{Ag}(T_1)$, $\mu_{AgCl}(T_1)$, $\mu_{Cl^-}(T_1)$ are the chemical potentials of silver, silver chloride, and chloride ion, respectively, at temperature T_1 ; F is the Faraday constant. In Eq.(1), $\Delta\phi_{TE}$, $\Delta\phi_D$, $\Delta\phi_{STR}$, and $\Delta\phi_{TD}$ are respectively the thermoelectric, diffusion, streaming and thermal diffusion potentials.

The experimental measurements have been carried out for two solutions: (X) $10^{-3}m$ HCl + $10^{-1}m$ NaCl and (S) $10^{-2}m$ HCl + $10^{-1}m$ NaCl at flow rates between 0.1 and $1.4\text{ cm}^3\text{ min}^{-1}$ and at temperatures of 25°C (18.7 MPa), 200°C (23.8 MPa), 350°C (24.2MPa), and 400°C (25.3 MPa). The measured values $\Delta E^{(1)} = E^{(1)}(S) - E^{(1)}(X)$, were respectively 57.3, 93.9, 123.1 and 135.4 mV at zero flow rate in the FTPHE.

If two different solutions are pumped through the Thermocell (I) and if one of them is assumed to be the test solution, X, and another one to be the standard solution, S, the measured pH difference is expressed as:

$$\Delta pH_{OBS} = pH(X) - pH(S) = F\{\Delta E^{(1)} - [\Delta\phi_D(S) - \Delta\phi_D(X)]\}/(2.303RT) \quad (2)$$

Note, that the expression (2) is not valid unless the measurements are carried out at constant temperature with a fixed flow rate in the FTEPBRE and zero flow rate in FTPHE. Deriving Eq. (2) we have assumed that the concentration of the molecular hydrogen is the same in both the test and standard solution. It is interesting to note that Eq.(2) is similar to the expression recommended by IUPAC for operational pH measurements at low temperatures ($<100^\circ$). Therefore, the developed FTEC can be conventionally used as an operating system for high temperature pH measurements. We would like to stress that as IUPAC recommends, we do not need to know the absolute potential of the reference electrode, but we do require it to be stable and invariant from one test measurement to another at a given temperature and pressure. In our FTEC we should also keep the reference solution flow rate constant. In addition, we need to have available standard pH solutions whose pH are known a priori. The dilute solutions of HCl(aq) and NaCl(aq) or their mixtures with NaCl(aq) can be used as the standard pH solutions at temperatures above 200°C . An important difference between our approach and the one which is proposed by IUPAC (for low temperature pH

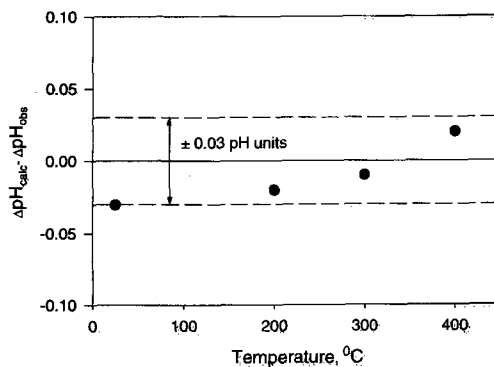


FIG. 1. Comparison between theoretically calculated and observed differences in pH, $[\Delta pH_{CALC} - \Delta pH_{OBS}]$ of the Thermocell (I).

measurements) is the diffusion potential term in Eq.(2). It is common practice in subcritical work to suppress the diffusion potential by employing a high concentration ($>3.5\text{ m}$) of KCl, because of the closeness equality of the transport numbers of K^+ and Cl^- ; however, this is only effective if the test solution is dilute. This is not easily accomplished at supercritical temperatures because of a possible phase-separation of highly concentrated solutions that might be employed in the reference electrode internal compartment. For example, in the case of NaCl, the highest possible concentration that one can have is about 0.1 m at temperatures up to 450°C and pressures up to 500 bar without having phase separation. However, this problem is mitigated by the fact that the transport numbers for Na^+ and Cl^- rapidly converge to the same value as the temperature exceeds 300°C and transitions across the critical point of water. The estimated values of $[\Delta\phi_D(S) - \Delta\phi_D(X)]$ in Eq.2 are -4.5 , -2.4 , -0.2 , and -0.01 mV respectively at temperatures 25°C (18.7 MPa), 200°C (23.8 MPa), 350°C (24.2MPa), and 400°C (25.3 MPa).

To demonstrate our approach for high temperature pH measurements, we calculated the pH difference, ΔpH_{CALC} , using the most accurate thermodynamic properties for HCl-NaCl- H_2O system and compared them with ΔpH_{OBS} data. It was found that the theoretically-calculated ΔpH_{CALC} values agree with the experimentally-derived ΔpH_{OBS} data to within ± 0.03 logarithmic units, and this comparison is presented in Fig. 1. Therefore, we conclude that the FTEC, developed in this work, is at an accuracy level where high quality potentiometric (better than ± 2.5 mV) and pH (better than ± 0.03 logarithmic units) measurements can now be carried out at temperatures extending into the supercritical region.