Potentiometric pH Measurements in High Subcritical and Supercritical Aqueous Solutions

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Abstract

An operational electrochemical thermocell is proposed for accurate potentiometric pH measurements in high subcritical and supercritical aqueous solutions. The thermocell consists of the silver-silver chloride flow-through external pressure-balanced reference electrode (FTEPBRE) and the flow-through platinum-hydrogen pH sensor. Using this thermocell we have measured the potentials of the thermocell for a few HCl(aq) and NaOH(aq) solutions of different concentrations and derived the corresponding pH differences (ΔpH) over a wide range of temperatures from 25 to 400°C. Comparison of the experimentally derived and theoretically calculated ΔpH values clearly demonstrates an ability of the thermocell to measure pH with a high accuracy (less than ±0.1 units), and this result in turn demonstrates the viability of the FTEPBRE as a versatile reference electrode for use at high subcritical and supercritical temperatures.

Keywords: supercritical aqueous solutions, pH measurements, reference electrode.

1. Introduction

A major barrier for studying many different technologically-significant physicochemical processes in aqueous systems at high subcritical and supercritical temperatures 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 standard thermodynamic properties. From a technological viewpoint, this knowledge would greatly aid progress in supercritical water oxidation technology; in controlling corrosion and mass transport in thermal (fossil and nuclear) power plant heat transport circuits; and in understanding and developing hydrothermal geochemistry, ore-forming processes, deep brines of sedimentary basins, nuclear waste disposal, and geothermal power plants.

In previous studies involving precise pH measurements in high temperature aqueous systems up to 300°C, Mesmer and co-workers [1] and Macdonald and co-workers [2, 3] investigated various aqueous solutions from 0 to 300°C using platinum-hydrogen [Pt(H_2)] electrodes as both the test and reference electrodes in concentration cells and the technique was very precise. The applicability of the Pt(H_2) electrode in high subcritical and supercritical aqueous solutions was demonstrated by Macdonald *et al.* [4], Hettiarachchi *et al.* [5], Macdonald *et al.* [6], and Ding and Seyfried [7, 8]. This electrode has been recently used to measure the Henry's Law constants for H_2(aq) [9] at temperatures up to 723 K. The Au(H_2) electrode has also been demonstrated as a Nernstian electrode in supercritical aqueous systems [10].

One of the most significant achievements in high temperature potentiometry was the development of the yttria-stabilized zirconia (YSZ) membrane sensor, which was demonstrated to be a primary (Nernstian) pH electrode for potentiometric measurements in high subcritical and supercritical systems [4-10] up to 450°C. However, all potentiometric techniques employ a reference electrode and, to date, it has been the accuracy of the reference electrode that has determined the accuracy of the measured potential, and hence pH. The critical role played by the reference electrode in determining the quality of potentiometric data is well recognized [11], and it is clear that little progress will be made in potentiometry in high subcritical and supercritical aqueous systems until an accurate reference electrode is devised. The main goal of the paper is to review advances that are being made in potentiometric and pH measurements in high subcritical and supercritical aqueous solutions and to demonstrate the current state-of-the-art.

2. Low temperature pH measurements

At low temperatures (<100°C), pH is determined with reference to a standard (buffer) solution, the pH of which we assume to be known. Thus, as noted in the IUPAC's Manual on Physical Chemistry Definitions [11], the pH of the test solution X is defined as

$$pH(X) = pH(S) + \frac{F(E_S - E_X)}{2.303RT} , \qquad (1)$$

for the following galvanic cell

Reference Electrode | KCl(aq, m>3.5 mol kg^{-1}) || Solution X | Pt/H_2 , (I)

where S is the pH of the standard solution, and E_S and E_X are the potentials measured against the same reference electrode. Thus, 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. We also need to have available standard buffer-solutions, whose pH is known *a priori*. We have adopted a similar approach with the advanced Flow-Through External Pressure-Balanced Reference Electrode (FTEPBRE), which is described in detail elsewhere [13].

3. Flow-through external pressure-balanced reference electrode

To achieve high accuracy in potentiometric measurements at high temperature, a reference electrode should meet the following requirements, which are considerably more stringent than those for ambient conditions: (1) resistance to chemical degradation; (2) tolerance to thermal and pressure (mechanical) stress; and (3) accurate resolution of measured potentials to ± a few mV.

The principle we adopted for the reference electrode is a flow-through technique, which can minimize interference from both contaminates (*e.g.*, corrosion products) and from the Soret effect, thereby providing a stable and highly accurate reference potential. As follows from our previous theoretical analysis of the thermal liquid junction potential problem [12], the FTEPBRE, in which the composition of the non-isothermal liquid junction is maintained accurately at a well-defined concentration, was considered to be an

appropriate way to solve the problem of performing accurate potentiometric measurements in high-temperature, high-pressure aqueous systems.

Briefly, the FTEPBRE employs techniques to minimize the effect of thermal diffusion on the reference potential, with the isothermal liquid junction potential being estimated from solution theory (see below). The unique feature of the FTEPBRE is that the reference solution flows through the electrode so that species concentrations across the thermal liquid junction are maintained constant [13]. Thus any tendency for thermal diffusion to occur is eliminated at the given temperature and pressure, and hence the electrode may be maintained in the stable Soret initial state.

4. High temperature pH thermocell

The silver-silver chloride/platinum-hydrogen, non-isothermal thermocell [13]

|<————— T_1 —————>|<—————————— T_2 ——————————>|<——— T_1 ———

Cu | Ag | AgCl | reference NaCl(aq) sol. ° test H^+(aq) sol. | H_2(Pt) | Pt ... Pt | Cu (II)

was employed for pH measurements in HCl(aq), NaOH(aq), HCl(aq)+NaCl(aq), and NaOH(aq)+NaCl(aq) solutions over wide ranges of temperature from 25 to 400°C and pressure from 250 to 350 bar. This cell exhibits great stability of the measured potentials (within ±5 mV) for long periods of time ranging from a few hours up to a few days.

A significant issue in high temperature pH measurements is the diffusion or isothermal liquid junction potential (ILJP). It is common practice [11, 14] in subcritical work to suppress the ILJP by employing a high concentration (>3.5 m) of KCl. 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 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 [15]. 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 value [16]. Accordingly, NaCl solution is of great interest for use as the reference electrode internal solution at elevated temperatures (300-450°C), because: (1) it emulates KCl in its transport numbers, and (2) the dissociation constant of NaCl(aq) is well known over wide ranges of temperature and pressure [16]. Note that there are no reliable conductivity or dissociation constant data for KCl(aq) solutions at the temperatures of interest, but the requisite data are available for NaCl(aq) solutions. Accordingly, for this latter system, the residual ILJP can be theoretically estimated, as is the common practice for high-accuracy work at ambient temperature, using the full expression for the liquid junction potential [17] as

$$E_D = -\frac{RT}{F}\sum_i \int \frac{t_i}{z_i} d\ln a_i \,, \tag{2}$$

where the summation is taken over all ions (activity a_i and valence z_i) in the junction with the integral being evaluated over the dimension of the junction, rather than by using the Henderson equation, which assumes ideality [17]. We have calculated the ILJP for the junctions of Termocell (II) [18], where 0.1m NaCl(aq) was used as the reference solution

and HCl(aq) or NaOH(aq) (with concentrations less then 0.01m) mixed with 0.1m NaCl(aq) were employed as the test solutions. It was found that the ILJP is of the same order as that at ambient temperature, because the increase in *RT/F* with increasing temperature is compensated for by the decrease in the summed quantities (note that for a 1:1 electrolyte z_1=1, z_2=-1 and $t_1 \rightarrow t_2$ and $a_1 \rightarrow a_2$ as the concentration decreases and the temperature increases). Our calculations show [18] that the values of E_D for Thermocell (II) range from a few mV to more than 10 mV. While not large, they are significant, and the accurate determination of pH requires correction of the reference electrode potential for this effect using Eqn. (2).

Dilute HCl(aq) and NaOH(aq) solutions were chosen for our first experimental studies because: (1) the dissociation constants data are available for temperatures up to at least 400°C; and (2) they are sufficiently dilute that activity coefficients can be estimated using extended Debye-Huckel theory.

5. Results of measurements

We have measured the potentials of Thermocell (II), $E^{(II)}$, for HCl(aq) and NaOH(aq) solutions of different concentrations. Because the thermodynamics of these solutions are well known over the entire temperature range of interest, one of them was assumed to be the test solution, *X*, and another one the standard solution, *S*. The measured pH difference is then expressed as

$$\Delta pH_{obs} = [pH(X) - pH(S)]_{obs} = \frac{F\Delta E^{(II)}}{2.303RT} - [E_D(S) - E_D(X)] \ , \qquad (3)$$

and are presented in Table 1. The values $E_D(S)$ *(i=S or X)* in Eqn. (3) are the isothermal liquid junction potentials between the standard and test solutions of Thermocell (II) at temperature T_2, which can be either experimentally suppressed using supporting electrolyte or theoretically calculated [by Eqn.(2)] if we know the equivalent conductances and concentrations of the species of both standard and test solutions [18]. The experimental values of $\Delta E^{(II)} = E^{(II)}(S) - E^{(II)}(X)$ were calculated using the experimental data taken from Ref. [13].

6. Discussion and conclusions

The difference in pH of the test, *X*, and standard, *S*, solutions in Eqn. (3), $\Delta pH_{obs} = [pH(X) - pH(S)]_{obs}$, can be calculated theoretically, and the comparisons between the observed and calculated values are then used to check the accuracy of the FTEPBRE. The calculated difference in pH, $\Delta pH_{calc} = [pH(X) - pH(S)]_{calc}$, is expressed as

$$\Delta pH_{calc} = \lg \frac{m_{H^+}(S)}{m_{H^+}(X)} \frac{\gamma_{H^+}(S)}{\gamma_{H^+}(X)} . \tag{4}$$

where $m_{H^+}(S)$ and $m_{H^+}(X)$ are the concentrations of H^+(aq) ion in the standard and test solutions, respectively, and $\gamma_{H^+}(S)$ and $\gamma_{H^+}(X)$ are the activity coefficients of H^+(aq).

For calculating $m_{H^+}(S)$ and $m_{H^+}(X)$, we solved the speciation problem for each solution given the total (stoichiometric) composition, temperature, and density. In doing so, we considered the following dissociation equilibria in describing the system:

$H_2O(l) \leftrightarrow H^+(aq) + OH^-(aq)$,

$HCl^0(aq) \leftrightarrow H^+(aq) + Cl^-(aq)$,

$NaCl^0(aq) \leftrightarrow Na^+(aq) + Cl^-(aq)$,

$NaOH^0(aq) \leftrightarrow Na^+(aq) + OH^-(aq)$,

together with the electroneutrality and mass balance constraints. The activity coefficients of the ions ,γ_i, were calculated using the second-order approximation of the Debye-Huckel theory.

It was found that the theoretically-calculated values, ΔpH_{calc} agree with the experimental data, ΔpH_{obs}, to within ±0.1 decimal logorithmic units, and this comparison is presented in Figure 1. We emphasize, however, that the difference between the measured and calculated potentials should not be attributed to the reference electrode alone, because Eqns. (3) and (4) contain parameters (*e.g.*, the activity coefficients and isothermal liquid junction potentials) whose uncertainties could easily account for the measured differences. Therefore, we conclude that the results of our measurements demonstrate the viability of the FTEPBRE, and we submit that the reference electrode developed in this work is sufficiently accurate (within a few mV) that high quality

potentiometric measurements can now be made at temperatures extending into the supercritical region.

Acknowledgments

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Figure captions

Figure 1. Comparison between theoretically calculated and experimentally measured differences in pH, [ΔpH_{calc} - ΔpH_{obs}] of the Thermocell (II).

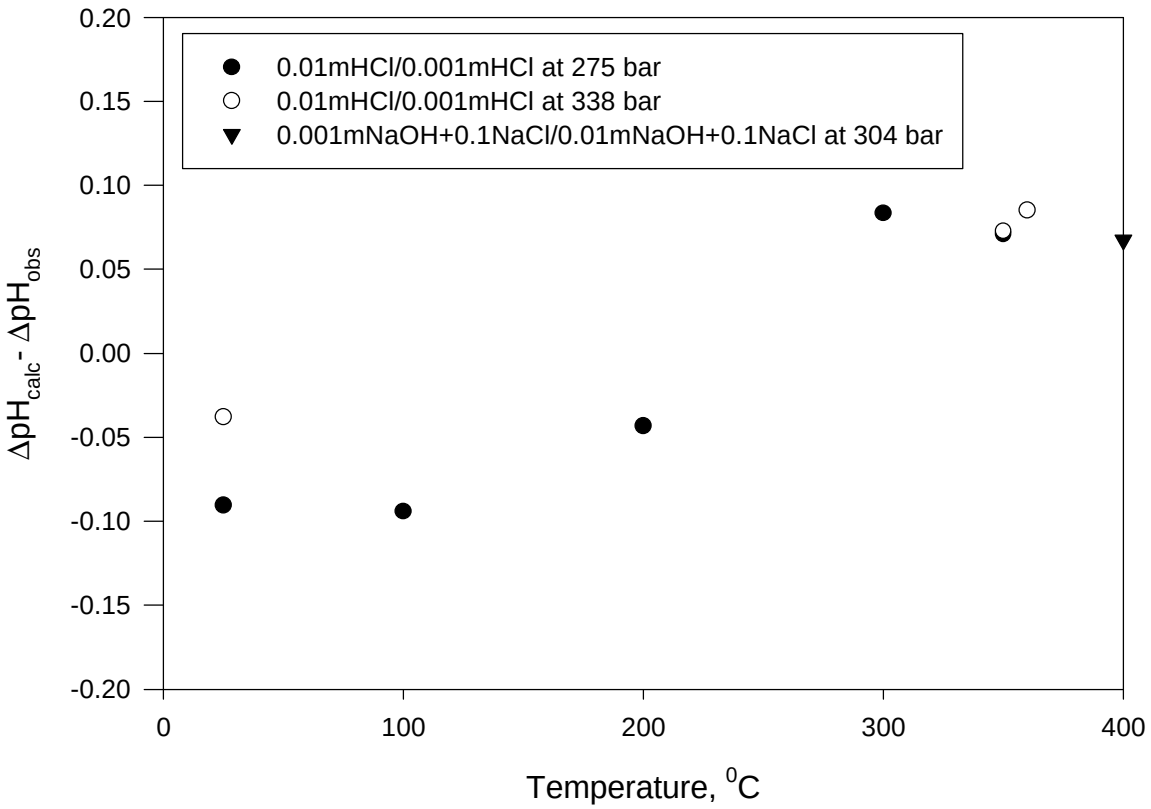
0.01mHCl/0.001mHCl at 275 bar
0.01mHCl/0.001mHCl at 338 bar
0.001mNaOH+0.1NaCl/0.01mNaOH+0.1NaCl at 304 bar
0.20
0.15
0.10
0.05
0.00
-0.05
-0.10
-0.15
-0.20
ΔpH_calc - ΔpH_obs
0
100
200
300
400
Temperature, 0C

Fig. 1

Table 1. Experimental data of ΔpH_{obs} obtained using measured potentials of thermocell (II) and Eqns.(2) and (3).

Temperature, °C	Pressure, bar	Solution X	Solution S	$-\Delta pH_{obs}$
25	275	0.01m HCl	0.001m HCl	1.090
100	275	0.01m HCl	0.001m HCl	1.094
200	275	0.01m HCl	0.001m HCl	1.042
300	275	0.01m HCl	0.001m HCl	0.882
350	275	0.01m HCl	0.001m HCl	0.755
25	338	0.01m HCl	0.001m HCl	1.038
350	338	0.01m HCl	0.001m HCl	0.786
360	338	0.01m HCl	0.001m HCl	0.730
400	304	0.001mNaOH+ 0.1mNaCl	0.01m NaOH+ 0.1mNaCl	0.928