Measurement and Control of pH in Hydrothermal Solutions

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Abstract: Hydrogen-electrode concentration cells with liquid junction are routinely used to measure the $\text{pH} = -\log[\text{H}^+]$ of aqueous solutions from 0 to 300°C. Results include the dissociation constants of common acids and bases, and the hydrolysis and complexation of metal ions in aqueous electrolytes over a wide range of salinities. Recently, we have utilized these cells to examine the sorption of H^+ on mineral surfaces, the solubility of minerals with continuous *in situ* pH measurement, and the thermal decomposition rates of organic acids.

1 INTRODUCTION

The pH is often considered the master variable of an aqueous system controlling the nature of dissolved aqueous species, the rates of homogeneous and heterogeneous aqueous reactions, the solubility and adsorptivity of rock minerals, the transport and deposition of contaminants and ore components, and the volatility of mineral and organic acids.

Measurement of the H^+ activity or concentration in aqueous solutions using conventional glass combination electrodes is limited to about 130°C, and is rarely performed at temperatures above 90°C due to the instability and fragility of either the glass membrane, the reference electrode, or the liquid junction.

Efforts to develop partially stabilized cubic zirconia pH electrodes for operation in the 100 to 400°C range continue (cf. MacDonald et al., 1992), but the reproducibility of pH measurement with zirconia membranes is presently limited to about 0.1 to 0.2 log units. Potentiometric measurements of pH at elevated temperatures were pioneered at Oak Ridge National Laboratory with the early efforts of Milton H. Lietzke and coworkers (eg., Lietzke, 1955), who employed Pt- H_2 electrodes coupled with Ag/Ag-salt reference electrodes to investigate the thermodynamic properties of HCl and other strong acids in electrolytes to 225°C, in cells without liquid junction. Because of the lack of a reliable reference electrode for high

temperature studies above about 200°C, Mesmer et al. (1970) developed a hydrogen electrode concentration cell which employs two identical Pt- H_2 electrodes, one immersed in the solution of interest, and the other immersed in a reference solution of known $[\text{H}^+]$ or $[\text{OH}^-]$, with both solutions connected by a porous liquid junction and exposed to the same H_2 partial pressure. Later, a "flowing emf cell" (Sweeton et al., 1973) was developed for studies of volatile reactants. The reduction of potentiometric data from such cells to extract quantitatively the stoichiometry and formation constants of aqueous protolytic reactions was formalized by Baes and Mesmer (1976). Cells of this type have been used for more than 30 years at Oak Ridge to obtain a wealth of highly precise data on the dissociation constants of mineral and organic acids and bases, the hydrolysis of metal ions, and the complexation of metal ions by aqueous anions, in the 0-300°C range, in 0-5 molal NaCl and KCl media, as well as in "non-complexing" media, such as tetramethylammonium chloride, sodium trifluoromethanesulfonate, etc. (see categorical bibliography in REFERENCES). Results using similar cells have been reported by D.D. MacDonald (eg., MacDonald et al., 1973), B.A. Bilal (eg., Bilal and Mueller, 1993), Y. Matsushima (eg., Matsushima et al., 1988), Shoesmith and Woon (1976), and Giasson and Tewari (1978).

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2 DISCUSSION

Figure 1 shows a schematic of an inexpensive Pt-H₂ concentration cell constructed from commercial components and suitable for operation to 100°C (Narkhede et al., 1994). The high temperature cells are operationally similar, although entirely composed of platinum and Teflon inner parts and housed in Hastelloy pressure vessels. The seals around the Teflon-sheathed Pt electrodes in the high temperature cells are now made with Teflon ferrules in tube extensions outside the furnace or bath (Wesolowski et al., 1984). Titrant solutions can be delivered to the test solution through platinum or PEEK tubing from a Zircalloy-body positive displacement pump, with a precision of ± 0.001 mL. A platinum or Teflon dip-tube can also be immersed in the test solution for periodic sampling, without affecting the cell response. The cell is placed within a thermostatted water bath (0-100°C), oil-bath (75-300°C), or aluminum-block furnace (50-300°C) to avoid temperature gradients. At the start of an experiment, the cell is purged with high-purity H₂ gas repeatedly and allowed to equilibrate at temperature under 1-10 bars excess H₂ pressure.

The simplest example of the use of these cells is the determination of the dissociation constant of a weak, monoprotic acid (HA). The cell configuration is

So long as $[\text{NaCl}]_1 \approx [\text{NaCl}]_2 \gg [\text{HA}] \approx [\text{NaA}] \approx [\text{HCl}]$, the potential between the electrodes is given by the Nernst equation

$$\Delta E = -(RT/F) \ln([H^+]_{\text{test}}/[H^+]_{\text{ref}}) + E_{ij},$$

where $[H^+]$ is the stoichiometric molality of H⁺, R and F are the Gas and Faraday constants, and T is the absolute temperature. When the supporting electrolyte (NaCl in this case) is ca. 50 to 100 times more abundant than any other ion, the liquid junction term (typically 1 millivolt or less) can be reliably approximated, and $\gamma H^+_{\text{test}} \approx \gamma H^+_{\text{ref}}$. From the measured $[H^+]_{\text{test}}$ together with mass- and charge-balance constraints, the molal dissociation constant (Q_{HA}) for the acid at the studied ionic strength can be calculated, typically with an accuracy of about ± 0.01 log units. By varying the total ionic strength from ca. 0.1 molal to 5-6 molal, the

Fig. 1: A Pt-H₂ concentration cell for studies to 100°C (Narkhede et al., 1994).

pK value and activity coefficient ratio for the dissociation reaction can be obtained by regressing the equation $\log Q_{\text{HA}} = \log K_{\text{HA}} - \log(\gamma H^+ \gamma A^- / \gamma HA)$ using an appropriate activity coefficient model like the Pitzer ion interaction treatment (with the assumption that compounds like NaCl, NaA and HCl completely dissociate in water). Alternatively, because the electrodes each respond to the activity of H⁺, one could choose to use a fully speciated solution model (incorporating ion pairing and a simplified extended-Debye-Hückel term) and calculate aH^+_{ref} , from which aH^+_{test} is again obtained from the Nernst equation.

By titrating solutions into the test cell at temperature, while maintaining nearly constant ionic strength, more complex protolytic equilibria can be studied, including the dissociation constants of polyprotic acids and the hydrolysis of metal ions ($xM^{z+} + yH_2O \rightleftharpoons M_x(OH)_y^{xz-y} + yH^+$). The complexation of metal ions by the anions of weak acids can also be studied by first determining the dissociation constants of the weak acid at the experimental conditions, and then monitoring the competition of H⁺ and M^{z+} for the acid anion. Because of the very precise data obtainable from such cells, it is possible to determine the complexation of metal ions by nonprotolytic ligands in solutions containing the anion of a weak acid which also complexes the metal of interest (Palmer

and Hyde, 1993). Even reactants unstable with respect to H_2 gas can be studied, so long as their reduction rates are sufficiently slow (Wesolowski et al., 1984; Palmer et al., 1987; Dickson, et al., 1990).

Recently, we have been employing Pt- H_2 concentration cells to study the adsorption/desorption of H^+ on rutile (TiO_2) surfaces at elevated temperatures (Machesky et al., 1994). The values of H^+ adsorbed/desorbed per unit of mineral surface area are reproducible and reversible (as evidenced by forward- and back-titration using acid and base titrants from two pumps). The results can be modeled to give insight into the nature of charged surface hydroxyl species and the structure of the aqueous medium adjacent to the surface. Also, by performing titrations over a range of ionic strengths at constant temperature, the pH of zero net surface charge (pH_{zpc}), an important variable in determining dissolution/precipitation rates, can be readily obtained.

Solubility studies are now underway with boehmite ($AlOOH$) at 100-250°C. Reversible and precise equilibrium solubilities have been obtained at all temperatures and ionic strengths studied, in experiments conducted in a specially-designed, large-volume concentration cell which has been run continuously for periods of over one month at temperatures to 250°C with no degradation of the electrode response or observable change in the reference solution composition. This approach shows great promise for determining the solubilities of pH-sensitive minerals, as well as the hydrolysis constants of metal ions which form insoluble oxides in aqueous solution (such as Fe^{2+} and magnetite). Furthermore, rates of precipitation and dissolution reactions involving H^+ can be directly observed in real time at experimental conditions without the need for sampling and chemical analysis of the solution.

Organic acids in sedimentary basin brines are under intense study by the geochemical community because of their potential role in generating secondary porosity, transporting ore and contaminant species, controlling mineral dissolution rates, and as precursors for natural hydrocarbon synthesis. We have initiated a detailed study of the rates of decomposition of oxalic and formic acid, using both conventional hydrothermal vessels, and Pt- H_2 concentration cells. The latter permits detailed accounting for the concentrations of the fully protonated acid and its anions (eg., formate, bioxalate, oxalate, etc.) without introducing additional

pH buffers. We have found that the decomposition rates of the fully protonated acids are orders of magnitude higher than those of the anionic forms. It is possible in some cases to calculate the concentrations of organic acid species from the measured pH together with mass- and charge-balance constraints, obviating the need for sampling and chemical analysis, and permitting real-time observation and calculation of instantaneous rates.

3 CONCLUSIONS

Many aqueous protolytic reactions can be studied experimentally to temperatures of 300°C with precise *in situ* pH monitoring, even over long periods of time (up to a month or more). We have demonstrated the utility of Pt- H_2 concentration cells, not only for homogeneous reaction measurements, but for heterogeneous studies of mineral solubility and adsorption. The large number of inorganic and organic acids and bases for which highly accurate dissociation constants at high temperature in dilute to concentrated salt solutions are now available also permits the design of experiments in which the pH is well-buffered by aqueous species, even if direct pH measurement is not employed. Furthermore, knowledge of acid dissociation constants at elevated temperatures permits determination of the pH of experimental solutions by less direct means, such as the measurement of the relative abundances of an acid/base pair by spectroscopic methods.

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