

## The Winner's Article of the First Dr. Masao Horiba's Award

### Development of Apparatus for Potentiometric pH Measurement for Supercritical Aqueous Solutions

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High-temperature and high-pressure water reaction fields including supercritical water have been aggressively attracting public attention in recent years as a new reaction field for synthesis, conversion, and reforming of chemicals. We have developed the most effective pH measurement method for understanding the information related to the solution environment of high-temperature and high-pressure water reaction fields. Particularly, we have been examining in detail, the following: strict temperature/pressure control, selection/design of electrodes, determination of electrode size/surface area, development of the contact method and liquid junction of the reference aqueous solution/test aqueous solution, pressure seals, etc. In addition to examining the corrosive protection/insulation equipment for the electrochemistry cell used for potential difference measurement. Consequently, we have developed equipment that allows pH measurement by the potential difference method using the same theory as used for normal temperatures.

#### Introduction

A supercritical fluid is a non-condensable fluid having the critical temperature  $t_c$  and critical pressure  $P_c$  peculiar to the substance and in the state where the temperature and pressure are more than these critical levels. By making the temperature and pressure into manipulation variables, the supercritical fluid density can be continuously controlled from a gaseous field to an aqueous solution field. Since a large change of the solvent characteristics can be expected in spite of there being only a single solvent, the supercritical fluid can be regarded as the new solvent which explodes the conventional concept of a solvent. Especially, supercritical water ( $P_c = 22.1$  MPa,  $t_c = 374$  °C) has in point the characteristic that the polarity of a solvent can be greatly controlled by manipulating the temperature or pressure<sup>[1]</sup>. The dielectric constant of water at normal temperature/pressure is approximately 80 but when the

near the critical point it is approximately 2 to 20. From the point of the dielectric constant, the supercritical aqueous solution can be considered as the sole organic polarity solvent that is stable at high temperature. Additionally the reaction equilibrium can be controlled through changing the dielectric constant by manipulating the temperature/pressure. The reaction controllability of critical water shows the flexibility of water as a solvent, and its engineering use is leading to innovative process development.

Recently the research related to the development of new chemical processes by positively utilizing the characteristics of supercritical water, such as:

- full oxidization (SCWO)<sup>[2]</sup> of persistent organic compounds
- non-catalytic organic synthesis<sup>[3]</sup>
- recovery of useful chemical materials from waste biomass<sup>[4]</sup>
- and the new chemical process of hydro thermal

synthesis of nano-sized metal oxides<sup>[5]</sup>. To put it in practical use, an understanding of the oxygen/acid reaction in the reaction field, the hydrolysis reaction of metal oxides, and the ion reaction equilibrium represented by the solution reaction of metal oxides is important. To accumulate this equilibrium constant data, a potential difference measuring method that can be used to evaluate hydrogen ionic activity is considered very important. However, conventionally, there are few examples of research that has taken to task the controllability characteristics of water in the supercritical field. This includes close to the critical point so therefore, the potential difference measuring method has not yet been established in this field.

The pH measuring method of high temperature solutions started with the silver-silver chloride electrode and, in addition to the potential difference measuring methods, (such as the platinum hydrogen electrode and YSZ film metal oxide electrode) more recently there was the in-situ UV/Vis spectroscopic-analysis method using a probe molecule. There are several reports of these methods in existence. In this paper, as the evaluation method of hydrogen ionic activity by potential difference measurement in high temperature high-pressure solutions includes the supercritical field, we focus on a pH measuring method that uses a platinum hydrogen electrode. This paper is an introduction to pH measuring equipment<sup>[6]</sup>, which we have developed, that uses a potential difference measuring method suitable for measurement at high temperatures, because the components ( $H_2$ ,  $H^+$ ) and electrode (platinum) which participate in the electrode reactions are thermally stable - although there are restrictions of hydrogen coexistence.

## Conventional Potential Difference Measurement in High Temperature High-pressure Water

The pH measurement equipment that uses the potential difference measuring method under saturated steam pressure normally uses a batch type device (Figure 1), the reference aqueous solution and test aqueous solution reside in the high-pressure container, and Teflon porous film is used as the liquid junction<sup>[7]</sup>. However, Teflon is heat resistant up to approximately 300 °C, and adding to

that, use in a high temperature field is difficult because substitutable ceramic film etc, has not been developed. The flow-through type method<sup>[8]</sup> was proposed to solve this problem. The conventional method that has been used is a cell having a T-shaped passage<sup>[9],[10]</sup>. Each end of the cell is the inlets of the reference aqueous solution and test aqueous solution respectively. The solutions are fed in with normal temperature contact at the center of the cell and discharged from the bottom. The reference electrode is located in the normal temperature part near the cell inlet where there is minimal influence from the temperature and pressure change. The indication electrode is located in the high temperature part near the center of the cell. Both electrodes use the platinum hydrogen electrode. This method allows potential difference measurement and does not require the physical liquid junction. However, the measurement is difficult to perform correctly due to the changing measured potential from the solution flowing into the circumference of the opposite poles. Additionally the flow potential (which is a function of the heat diffusion potential resulting from the difference in temperatures between the electrodes, the distance between electrodes and the flow rate) influences the measured potential, therefore, the flow rate dependence must be measured and functionally approximated for calculating the zero flow value, to remove the influence. This requires much time and these numerous development areas still remain.

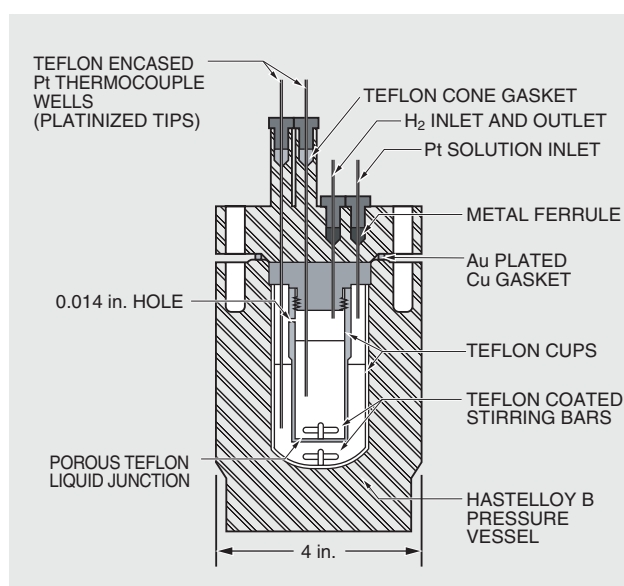


Figure 1 The Outline Figure of Batch Type Potential Difference Measuring Equipment

## Development of High Precision pH Measuring Equipment for Supercritical Solutions by Using the Potential Difference Measurement Method

The accuracy of the various physical-property values (dissociation constant, the electrical conductivity/transport number of ions, solubility, phase equilibrium) becomes indispensable when evaluating the soundness of equipment. This and the evolution of apparatus for developing pH-measuring equipment for supercritical solutions is very important. In supercritical solutions, reference values in HCl as acid and NaCl as unrelated salt are the most abundant. In this section, we describe the evaluation of physical-property values and then introduce the developed equipment.

### Evaluation of Physical-properties Value

Also in a supercritical solution system, Equation (1) describes potential difference  $\Delta E$  in the potential difference measurement using a platinum hydrogen electrode, based on Nernst's equation.

$$\Delta E = \frac{RT}{F} \ln \frac{m_{H^+, test} \gamma_{\pm, test} a_{H_2, ref}}{m_{H^+, ref} \gamma_{\pm, ref} a_{H_2, test}} + \Delta E_{LJ} \quad \dots (1)$$

However, the flow potential and heat diffusion potential are further added to the above-mentioned conventional flow-through type equipment<sup>[9],[10]</sup>.  $m_{H^+}$  is the hydrogen-ion density,  $\gamma_{\pm}$  is the average ion activity coefficient,  $a_{H_2}$  is the hydrogen activity, and  $\Delta E_{LJ}$  is the potential between solutions. Subscripts “ref” and “test” express the reference aqueous solution and test aqueous solution.  $\gamma_{\pm}$  and  $a_{H_2}$  are considered to be constant by adding the unrelated salt at the same concentration in the reference aqueous solution and test aqueous solution.  $\Delta E_{LJ}$  can be evaluated by the ion density in the solution from Henderson's equation and electrical conductivity data of each ion. Then, the dissociation equilibrium constant of the solute and electrical conductivity data is indispensable for the evaluation of the measured potential. Considering that the ion action including the reaction equilibrium in the supercritical solution can be described well as a function of temperature and water concentration, we presented the dissociation constants such as hydrogen chloride (HCl)

and sodium chloride (NaCl) and ion electrical conductivity data as a function of the temperature and water concentration<sup>[6]</sup>. As for the electrical conductivity, we calculated values of each ion using the transport number of each ion from the data of the ion pair.

### Improving the Accuracy of Flow-through Type Potential Difference Measuring Equipment

The manufactured equipment is shown in Figure 2 that solves a main problem in conventional equipment. The equipment is made of high corrosion resistance HASTELLOY C-276 (inner diameter: 4 mm). Zirconia (ZrO<sub>2</sub>) tube is used for the conventional equipment for corrosion protection and insulation between the electrode and cell, but considering that this line bears the brunt of the heated part of the solution, the alumina (Al<sub>2</sub>O<sub>3</sub>) tube (inside diameter: 2 mm) that has high corrosion resistance and high thermal conductivity is used to heat the solution more effectively. The platinum line (outside diameter: 0.5 mm) is used for the electrode, the tip of the measuring part wound in the shape of a coil is platinum black, the remaining high temperature part is the Al<sub>2</sub>O<sub>3</sub> tube (outside diameter: 1 mm, inside diameter: 0.6 mm). The low temperature part is covered with the heat shrink tube. The details of the electrode part are within the dotted lined ellipse in Figure 2(a) and are shown in more detail in Figure 2(b), with the details of the electrode shown in Figure 2(c).

The composition of the electrode is shown in Equation (2).



Reference aqueous solution: HCl ( $10^{-4}$  mol/kg) + NaCl ( $10^{-1}$  mol/kg)

Test aqueous solution: HCl ( $10^{-4}$  mol/kg or  $10^{-3}$  mol/kg) + NaCl ( $10^{-1}$  mol/kg)

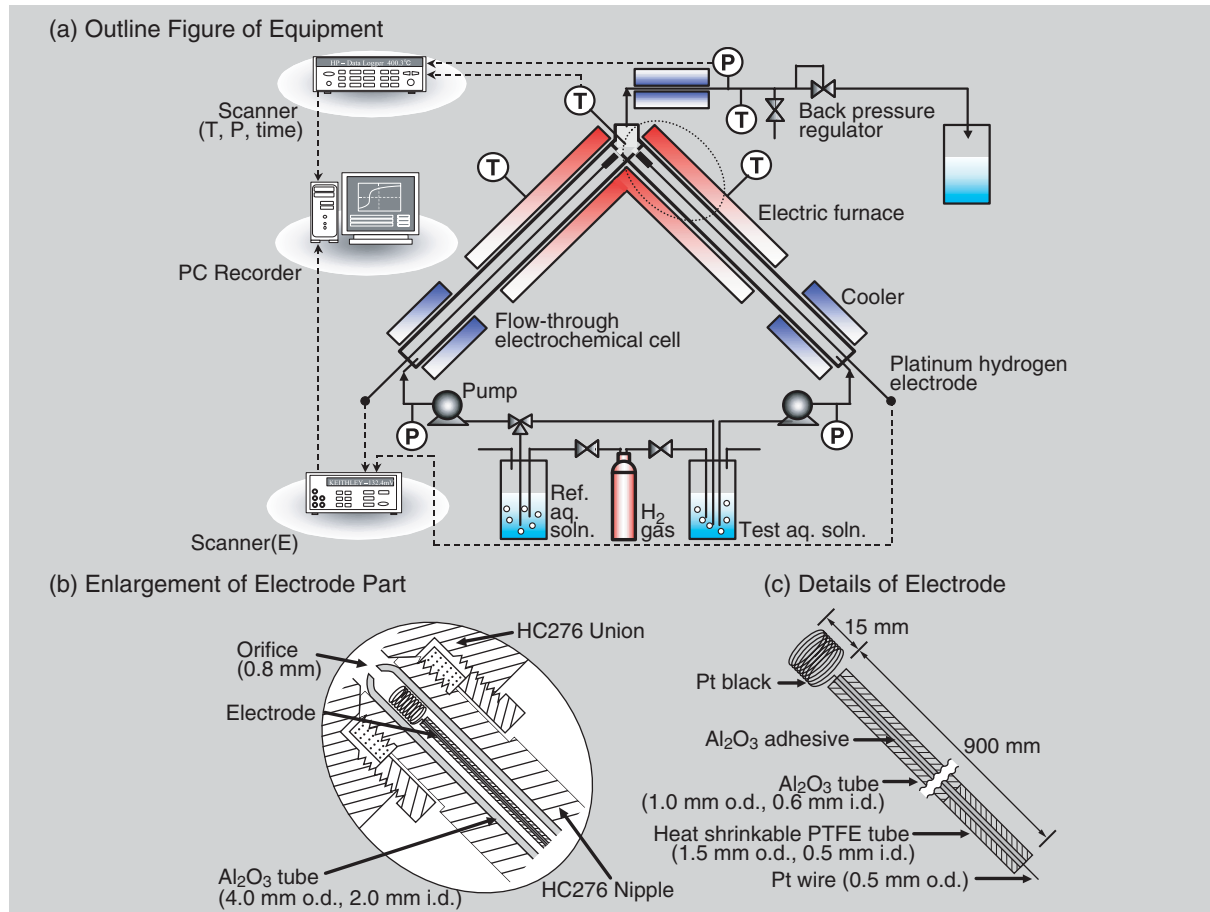


Figure 2 Flow-through Type Potential Difference Measuring Equipment

In the experiment, the reference aqueous solution and test aqueous solution were supplied respectively at the same flow rate using the HPLC pump and were introduced at the right and left of the cell. Then, they were heated to the predetermined temperature, and the potential difference measured while they were passing through the electrode of the cell center. Both solutions were contacted and collected after cooling and reducing the pressure. In advance of the actual experiment, at each measurement temperature, the temperature distribution in the cell and the relation between electrode surface area and equilibrium potential attainment time were analyzed, and the position and size of the electrode was determined. By locating the reference electrode in the high temperature part near the cell center, the same as for the indication electrode, the distance between electrodes was shortened

from the conventional 80 cm to 1 cm. Thereby, the heat diffusion potential and flow potential were successfully removed, and measurement at an arbitrary flow rate was attained. The volumes between electrodes were also improved from the conventional  $10.1 \text{ cm}^3$  to  $0.1 \text{ cm}^3$ , and the replacement speed of the solution was improved. In order to prevent concentration change generated by the inflow to the circumference of the opposite poles of the solution, the form of the cell was changed into a 'Y' shape from the original 'T' shape, the 0.8 mm orifice dia. was newly manufactured, and was located at the electrode tip. This achieved control of the measurement potential standard deviation - a sharp change from the conventional 2.3 mV to 0.4 mV. Thus, by using this version of the cell, the time required for data under a single condition was successfully shortened from dozens of hours to several hours.

Actually the potential difference was measured for the HCl + NaCl solution system in the temperature range of 19.6 °C to 392.9 °C and the pressure range from 0.1 MPa to 29.8 MPa. An example of the potential response in the potential difference measurement is shown in Figure 3, and the flow rate dependence of the potential difference measurement is shown in Figure 4. The solid line in Figure 4 shows the evaluated potential difference based on the Equation (1) according to the reference value. The pH of the test aqueous solution was calculated with a tolerance of ±0.02 in pH units from the measured potential and corresponded to the value calculated using:

- the reference value of the equilibrium constant
- the activity coefficient equation
- the flow-in/out of electric charge
- and flow-in/out of solutions.

This was considered to an acceptable tolerance for measurement accuracy under a high temperature and high pressure. Thus we consider that the direct measurement of exact pH in the supercritical solution is possible by using this method.

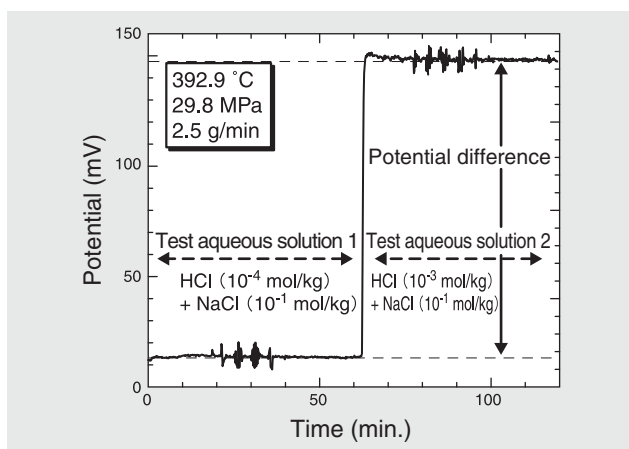


Figure 3 An Example of Potential Difference Measurement Result

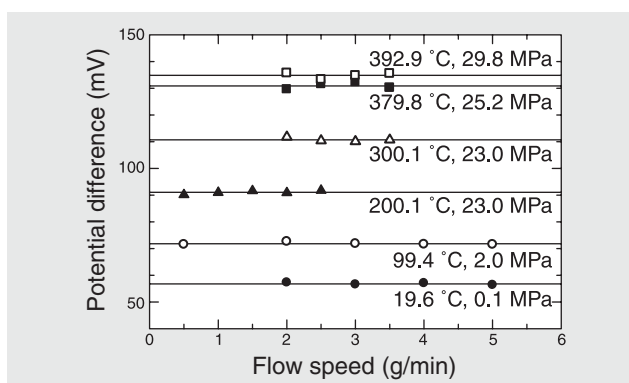


Figure 4 Flow Rate Dependence of Measured Potential Difference

### Potential Difference Measurement of Supercritical Acetic Acid Solution and Supercritical Sulfuric Acid Solution

Using the developed system, the potential difference between acetic acid (HAc)<sup>[11]</sup> solution and sulfuric acid (H<sub>2</sub>SO<sub>4</sub>)<sup>[12]</sup> in supercritical solution was measured, and the dissociation constant was determined. During measurement, the reference aqueous solution was HCl + NaCl, and the test aqueous solution was HAc + NaCl and H<sub>2</sub>SO<sub>4</sub> + NaCl. As an example, the temperature and the pressure dependence of the determined dissociation constant of the acetic acid are shown in Figure 5. The determined dissociation constant corresponded well to the reference value in the subcritical field. Also the dissociation constant was accurately determined even in the supercritical solution. The determined dissociation constant lowered in accordance with the temperature increase under constant pressure, and it decreased in accordance with the pressure reduction under the constant temperature. This was caused by the dielectric constant of the water.

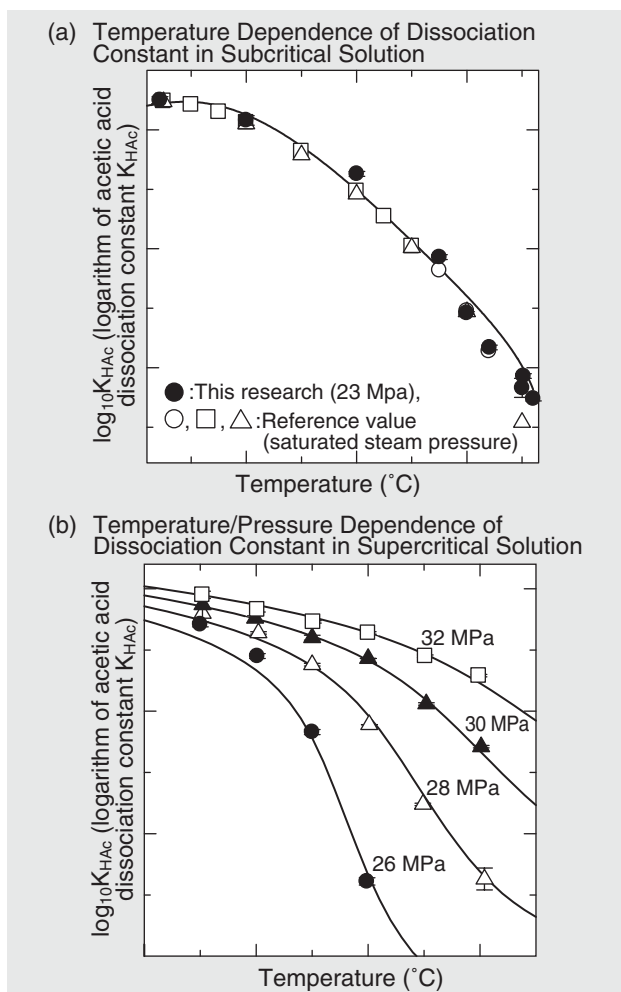


Figure 5 Determined Dissociation Constant of Acetic Acid

## Conclusion

In this paper, we introduced, focusing on our result, the present situation of the potential difference measurement method relating to the high temperature high-pressure solution including supercritical conditions using a platinum hydrogen electrode. In the future, we will proceed with research into the YSZ film metal oxide electrode which is not restricted by coexistence of hydrogen gas, unrelated salt, etc, and further improve accuracy and shorten measuring time. We will achieve this by development that focuses on the super critical solution system and additionally, minimizing the cell to an electrochemical microcell. Using this method, we will be able to evaluate hydrogen ion activity in various supercritical solutions and accumulate the ion reaction equilibrium data in the supercritical solution. This will surely enhance understanding the ion reaction equilibrium in high temperature high-pressure water, leading to a complete understanding of the solution chemistry.

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