Fig. 1, 4-necked ground glass joint flask cell

Fig. 2. Potential recovery curve of the homogeneous cell Pt(p) |H₃PO₄(0.980N)| Pt (bright) at 30°C under non-stirring condition.
Table 1

Results of the homogeneous cells at 30°C under H₂ gas (1 atm).

<table>
<thead>
<tr>
<th>Cell No.</th>
<th>Homogeneous cell</th>
<th>Constant potential (volt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pt(p)</td>
<td>H₂SO₄ (0.510N)</td>
</tr>
<tr>
<td>2</td>
<td>Pt(p)</td>
<td>H₃PO₄ (0.980N)</td>
</tr>
<tr>
<td>3</td>
<td>Pt(p)</td>
<td>KOH(0.328N)</td>
</tr>
</tbody>
</table>

p: platinized;  b: bright;  g: graphite
bright platinum. Thus the inequality (9) can be justified in this way.

It is interesting that the non-zero residual potential poses a serious question or paradox on the laws of thermodynamics. Let us consider there always exist a non-zero potential of the homogeneous cell, Pt (platinized) $| H_3PO_4$ under $H_2 | Pt$ (bright). Upon being discharged, there is a current flowing. According to Faraday's law, a current must accompany an electrochemical reaction at each electrode, so at the platinized platinum electrode, the only possible electrochemical reaction must be

$$H_2 \rightarrow 2H^+ + 2e^-$$

since the platinized platinum is the negative electrode of the cell. At the bright platinum electrode, the only electrochemical reaction must be

$$2H^+ + 2e^- \rightarrow H_2$$

There is no other electrochemical reactions possible on either platinized and bright platinum electrode, since $PO_4^{3-}$ is quite inert. The paradox is that the overall electrochemical reaction is a cyclic mechanism which is not tolerated by the laws of thermodynamics. This aspect has been long overlooked. More work and thoughts should be concentrated on this very important aspect of electrochemistry as well as thermodynamics.

References

(2) D. MacGillavry, ibid., 19, 1195 (1951).
If \( \frac{K_R}{K_0} = \frac{K'_R}{K'_0} \) holds, then the inequality (4) is solely due to the inequality (5). There are different concentrations of \( H_2 \) and \( H^+ \) on the surface of platinized and bright platinum. Thus the non-zero residual potentials can be explained by the different adsorption effects of different electrode surface conditions. This is consistent with the idea of adsorption potential. On the other hand, if \( \frac{C_{H^+}}{C_{H_2}} \) holds, the inequality (4) is solely due to the inequality (6). This means different rate constants on different electrode surface conditions. The present study can not determine which situation is correct.

Instead of molar concentrations. More rigorously, activities are used in equation (2) and (3), we obtain

\[
\Delta \phi = \frac{RT}{F} \ln \left( \frac{K_R}{K_0} \frac{a_{H^+}^2}{a_{H_2}^2} \right) \quad (7)
\]

\[
\Delta \phi = \frac{RT}{F} \ln \left( \frac{K'_R}{K'_0} \frac{a_{H^+}^2}{a_{H_2}^2} \right) \quad (8)
\]

Theremodynamically, if the homogeneous cell is in chemically equilibrium state, the activities of \( H^+ \) and \( H_2 \) are everywhere the same either on platinized or bright platinum. Therefore the inequality, \( \Delta \phi \neq \Delta \phi' \), is solely due to the inequality.

\[
\frac{K_R}{K_0} \neq \frac{K'_R}{K'_0} \quad (9)
\]

In view of the platinized platinum being the negative electrode of the homogeneous cell, it is easy to show the following equality is true

\[
\frac{K_R}{K_0} < \frac{K'_R}{K'_0} \quad (9)
\]

Kinetically, the rate-determining step of electrochemical oxidation of \( H_2 \) into \( H^+ \) is the dissociation of hydrogen molecule into two hydrogen atoms. The electro-catalyst, platinum black, is known to be more effective in decomposing \( H_2 \) into two \( H \) atoms than bright platinum. Thus \( K_0 > K'_0 \). On the other hand, the reduction rates of \( H^+ \) into \( H_2 \) can be considered about equal on the platinized and the
electrode. In the case of $\text{H}_2-\text{H}^+$ electrochemical equilibrium, the Butler-Volmer equation for the platinized platinum electrode is

$$i = 2Fk_0 c_{\text{H}_2} e^{(1-\beta) \Delta \phi / RT} - 2Fk_R c_{\text{H}^2+} e^{-\beta \Delta \phi / RT}$$  \hspace{1cm} (1)$$

where $k_0$ and $k_R$ are the rate constants of oxidation and reduction, respectively; $\Delta \phi$ is the metal-solution potential. If the platinized platinum electrode is open-circuited, there is no current flowing, i.e. $i=0$, so that it is obtained from equation (1) the following equation

$$K_0 c_{\text{H}_2} e^{\Delta \phi / RT} = k_R c_{\text{H}^2+}$$

or

$$\Delta \phi = \frac{RT}{F} \ln \frac{k_R c_{\text{H}^2+}}{K_0 c_{\text{H}_2}}$$  \hspace{1cm} (2)$$

Similarly for the bright platinum, it can be obtained as

$$\Delta \phi' = \frac{RT}{F} \ln \frac{k'_R c'_{\text{H}^2+}}{K'_0 c'_{\text{H}_2}}$$  \hspace{1cm} (3)$$

It is experimentally found that the metal-solution potential of the platinized and bright platinum is different, i.e. $\Delta \phi \neq \Delta \phi'$. Thus equations (2) and (3) lead to the following inequality,

$$\frac{k_R c_{\text{H}^2+}}{K_0 c_{\text{H}_2}} \neq \frac{k'_R c'_{\text{H}^2+}}{K'_0 c'_{\text{H}_2}}$$  \hspace{1cm} (4)$$

The inequality (4) is due to the inequality

$$\frac{c_{\text{H}^2+}}{c_{\text{H}_2}} \neq \frac{c'_{\text{H}^2+}}{c'_{\text{H}_2}}$$  \hspace{1cm} (5)$$

or

$$\frac{k_R}{K_0} \neq \frac{k'_R}{K'_0}$$  \hspace{1cm} (6)$$

or both inequality (5) and (6)
Our purpose of this study is to find out whether the potential of hydrogen-hydrogen ion equilibrium at the inert substrate metal can be influenced by the surface conditions (bright or platinized) of the platinum electrode and the electrode material such as graphite under the equilibrium condition. Using the suitable electrolyte H₃PO₄, a constant potential of 0.371 volt was found with bright platinum as the positive electrode. According to MacGillavry's explanation, since hydrogen-dydrogen ion equilibrium can not be readily established at the bright platinum, it is an irreversible electrode which might not obey Nernst equation. Therefore the adsorption potential (as used by MacGillavry) between metal and solution of the irreversible electrode might be different from that of the reversible potential of platinized platinum. This is indeed confirmed by the present investigation. Although sulfuric acid is not so inert (might be reduced by H₂, but after long discharge or standing, sulfate-sulfite equilibrium could also be reached), large residual potential of 0.526 volt was obtained. In the case of using KOH, the electrochemical reaction at the two electrodes is different from other two cells as following:

\[ 
H_2 + 2 \text{OH}^- \rightleftharpoons 2 \text{H}_2\text{O} + 2 \text{e}^- 
\]

The above electrochemical equilibration can be accelerated by platinized platinum, but not by bright platinum or graphite. So there is potential difference between the platinized platinum and bright platinum or graphite.

It was also found that the residual potential between the platinized platinum and no-heat-treated bright platinum was less than that of the platinized platinum and heat-treated bright platinum. This indicates that the electrode of heat-treated bright platinum is more irreversible than no-heat-treated platinum because of the smooth surface of heat-treated platinum. Therefore it is plausible that the active sites which catalyze the \(H_2-\text{H}^+\) electrochemical equilibrium is the edges or defect areas of platinum metal. The smooth surface of bright platinum is most ineffective in catalyzing \(H_2-\text{H}^+\) electrochemical equilibrium.

Although there is a controversy\(^8\),\(^9\),\(^10\) about the validity of Butler-Volmer equation\(^11\), it is still the best model for predicting the kinetic behavior of
The results of the three cells using \( \text{H}_2\text{SO}_4 \), \( \text{H}_3\text{PO}_4 \) and KOH are shown in Table 1. For cell No. 1 using sulfuric acid, a constant potential of 0.526 volt was found which is the highest potential among the cells investigated. With phosphoric acid which is a weaker acid, the constant potential of cell No. 2 was found to be 0.371 volt at 30°C. For the cell No. 3 using potassium hydroxide, three electrodes were used, the results are that the constant potential of bright platinum is 0.496 volt, that of graphite is 0.460 volt relative to platinized platinum electrode. It must be noted that the potentials of these three cells were higher at the beginning of the discharge and then gradually decreased to the constant potentials as shown in Table 1. The platinized platinum electrode was the negative electrode in all the three cells.

Discussion

The three electrolytes \( \text{H}_2\text{SO}_4 \), \( \text{H}_3\text{PO}_4 \) and KOH used here are considered to be relatively inert electrolytes. It is known that \( \text{CN}^- \), \( \text{Cl}^- \), \( \text{Br}^- \) or \( \text{I}^- \) etc. can react with the metals such as Cu, Hg, Ag and even with Pt. Therefore halide and cyanide electrolytes were not used here. Phosphoric acid is the best electrolyte in the present investigation, since \( \text{PO}_4^{3-} \) could neither react with platinum, nor to be reduced by hydrogen. Although \( \text{SO}_4^{2-} \) can not react with platinum, but it could be reduced by hydrogen gas as the following reaction

\[
\text{SO}_4^{2-} + \text{H}_2 + 2\, \text{H}^+ \rightarrow \text{H}_2\text{SO}_3 + \text{H}_2\text{O}
\]

since the reduction potential of \( \text{SO}_4^{2-} \) in acid solution is \( E^0 = 0.17 \) volt.\(^7\) As for hydroxide ion \( \text{OH}^- \), it could react with platinum, but could not dissolve platinum unlike hydrochloric acid which can dissolve platinum to become \( \text{PtCl}_6^{3-} \) ion. If \( \text{PtCl}_6 \) is present in the solution, it can be deposited on the bright platinum because the bright platinum is the positive electrode of the cell, thus the bright platinum becomes more or less platinized. So the residual potential of homogeneous cell using \( \text{HCl} \) solution is about 0.10 volt less than that using \( \text{H}_3\text{PO}_4 \) solution. The experimental from the homogeneous cell using \( \text{HCl} \) solution will be reported later.
potential to be measured, the electric wires connecting the electrodes were removed and the potential was allowed to recover. Then under non-stirring condition, open-circuit potential was measured with YEW Type 2722 DC Potentiometer. A typical potential recovery curve is shown by Fig. 2. After each experiment, the concentration of the solution in the flask was determined by acid-base titration.

The chemicals H₂SO₄, H₃PO₄ and KOH used here are all of reagent grade. Water was triply distilled. High purity Marz grade Pt wire obtained from Material Research Corporation was used here. Two different surface treatments of platinum electrodes were made. The Marz grade platinum wire to be used as the bright platinum electrode was heated in a Bunsen flame to red hot and cooled in the air. The heat-treated platinum wire appears softer and brighter, apparently the surface of the platinum wire was more smooth and less strained. The platinized platinum electrode was obtained by electrolyzing in 2% chloroplatinic acid solution as the negative pole. No lead acetate was used here. Graphite electrodes were spectral grade graphite rod with diameter 0.6 cm and length 3.7 cm. The graphite rod were obtained from Applied Research Laboratories Inc. which supplied the material for emission spectrographic analyzer.

Results

After completion of hydrogen bubbling, each cell was first discharged continually for 10 days, only occasionally open-circuited for potential measurement. Then connecting wires were removed, the open-circuit potential would gradually recover as the typical potential recovery curve of Fig. 2. It usually took several hours to completely recover. In order to know whether the homogeneous cells reached the equilibrium state or not, the cell was discharged again for about 15 hours (overnight) and open-circuited to wait until the cell recovered to their constant potentials, then the potential was measured. Usually the discharge operations were repeated at least 5 times. If no decreasing tendency of the potential was found, then it was sure that the constant potential was reached.
Experimental

The apparatus used was a 4-necked ground glass joint 250 ml flask fitted with different glass equipments as shown by Fig. 1. The central outlet and one of the side outlets were fitted with the glass stoppers with coarse platinum wire passing through them. The low end of the coarse platinum wire can be fastened with aid of a fine platinum wire or spot-welded with a spiral metal wire to be used as the electrode. The other two side outlets were fitted with gas-incoming and gas-outgoing traps. The traps were filled with the same solution as that in the flask. The no-leakage structure of this apparatus was further assured by covering the four outlets with vaseline. In this experiment, 5-necked ground glass joint 250 ml flask was also used, the additional outlet was for a third electrode. The present apparatus is the improved version of previous one reported before.

50 ml of solution to be investigated was placed into the 4-necked or 5-necked flask immersed in a thermostat controlled within 0.1°C. In order to minimize air dissolved in the solution, the distilled water used to prepare the solution was boiled or degassed under reduced pressure at first. Hydrogen gas which was generated by electrolyzing 15% NaOH solution was passed through vanadous chloride solution to remove oxygen in the gas stream. The flask was first evacuated by an aspirator and hydrogen gas was bubbling into it. This was repeated several times. Finally, hydrogen gas was continually bubbling into the flask at least one hour to assure the complete absence of air in the flask. When the bubbling of hydrogen gas was completed, hot liquid vaseline was poured into the outlet cups of the flask to serve as sealing material when it solidified. Then this homogeneous cell was ready for discharge.

To discharge the cell, the two electrodes or three electrodes were connected with electric wires for a sufficiently long time. In order to find out the difference in approaching the equilibrium state, some of the solutions were magnetically stirred; some of the solutions were not magnetically stirred. It was found that the equilibrium state can reach in the unstirred flask in a reasonable time (about 10 days), but in slower rate than stirred flask (about 5 days). When open-circuit
as adsorption potentials which do not obey the Nernst equation. Young and co-worker\(^3\) has measured the open-circuit potentials of hydrogen electrode with different substrate metal and correlated the potentials with their d-band structure. It was assumed that open-circuit polarization, measured as the deviation from reversible potentials, is a measure of the energy loss caused by irreversible chemisorption at electrode. Mixed potential theory\(^4,5\) has also been employed to explain the potential deviation.

The conventional method of measuring the open-circuit potential of a single electrode is done by dipping the sample electrode in a solution and its potential is measured relative to a reference electrode connecting the solution with a salt bridge. Most of the steady potentials of single electrode were done in this way. The conventional method is subjected to some difficulties. First, liquid junction potential of salt bridge is not completely negligible and also susceptible to the nature of solution used. Secondly, KCl in the salt bridge would slowly diffuse to the solution, therefore there is time limit before a reliable steady potential can be measured. In view of these difficulties, present experiment constructs a new type of electrochemical cell which itself is a closed system and free of liquid junction. As an example, the cell \(\text{Pt (platinized)} | \text{H}_3\text{PO}_4 \text{ under H}_2 \text{ gas} | \text{Pt (bright)}\) consists of two electrodes dipped into a homogeneous phosphoric acid solution which is covered by hydrogen gas. This kind of cell construction is called homogeneous cell. One electrode of the cell is platinized platinum. It behaves as a reversible hydrogen electrode and its potential can be predicted by the Nernst equation. Other electrode is bright platinum at which the hydrogen-hydrogen ion equilibrium can not be readily established. According to MacGillavry’s explanation, it is a polarizable (irreversible) electrode, which the Nernst equation might not hold. Therefore the metal-solution potential at the platinized platinum electrode might be different from the metal-solution potential at the bright platinum electrode, that is, the homogeneous cell could have a non-zero residual potential. The present study found that homogeneous cells have non-zero residual potentials, after the exhaustive discharge.
A Study of Hydrogen-Hydrogen Ion Electrochemical Equilibrium on the Different Surface Conditions of Substrate Metals

Tzu Fang Lin

Department of Chemistry
National Taiwan Normal University

ABSTRACT

The homogeneous cells were constructed by dipping two electrodes of different surface conditions into a homogeneous solution and covered by hydrogen gas. Through the exhaustive discharge, the equilibrium state can be reached inside the homogeneous cells and constant residual potential were measured. This study is concentrated on hydrogen-hydrogen ion electrochemical equilibrium on different surface conditions of substrate metals. Large residual potentials were found for the homogeneous cells consisting of reversible hydrogen electrode and irreversible hydrogen electrode. Although the nonzero residual potentials can be explained by adsorption or electric double layer effect, the question whether the non-zero residual potential can be justified in terms of the principles of thermodynamics remains open.

Introduction

MacGillavry\textsuperscript{1,2} has investigated the properties of the metal-solution potentials of nickel in nickel-free hydroxide and phosphate solution. He found that the steady potentials of the metal-solution do not obey the Nernst equation. He concluded that the Nernst equation is only applicable to the unpolarizable (reversible) electrodes at which there exist electrochemical equilibria due to mechanisms of reversible transfer of some ions between the electrode and solution. In the absence of any electrochemical equilibria, the metal-solution potentials are interpreted