STUDIES ON THE KINETICALLY EQUILIBRIUM POTENTIALS OF MERCURY AND PLATINUM ELECTRODES IN HOMOGENEOUS CELLS

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ABSTRACT

Several homogeneous cells with mercury and platinum electrode were inves.igated. By using stress-free liquid mercury electrode, it was thought that the equilibrium could be reached in a shorter time and finally the residual potentials of the cells were zero. Although it took shorter equilibration time, the residual potentials were not zero. In this report the different magnititude of observed electrode potential are explained. A new concept of kinetically equilibrium potential (K. E. P.) which differs from the concept of thermodynamically equilibrium potential (T. E. P.) is also introduced. An inevitable conclusion that most of homogeneous cells have non-zero residual potentials can be drawn from different structures of electric double layer for different electrodes even in the equilibrium state.

Introduction

It has been known for many years that the potentials of hydrogen electrodes are quite different on different substrate metals or even same metal, but of different surface states. These phenomena were observed by Plzak[1], Beans and Hammet[2], Ives el.al.[3] and Young[4]. We have also reported the results of the investigation on potentials of hydrogen electrodes on different surface conditions of substrate metals.[5] A large potential difference of about 0.45 volt between the hydrogen electrodes of very bright platinum and platinized platinum were observed using different electrolytic solutions. Recently we have found that there is a persistent potential of 300 mv between hydrogen electrodes with substrate metal gold and platinum (half-platinized); 270 mv between gold and graphite electrodes.[6] The persistent potential maintained more than ten months without decreasing tendency in a closed homogeneous cell using gold and platinum (half-platinized) electrode.

Another notable potential discrepancy between the observed rest potential and reversible potential is oxygen electrode. Rest potential of oxygen electrode with substrate metal platinum is 1.06 volt[7] quite different from thermodynamically calculated equilibrium potential 1.229 volt. With different substrate metals or different surface conditions, different potentials of oxygen electrodes were observed.[8] We have also studied some homogeneous cells using copper electrode with differen electrolytic solutions and found that the residual potentials of these cells were not zero.[9,10]

In this report, the homogeneous cells using mercury electrodes will be mentioned. Mercury used as the electrode in this kind of investigation has some advantages: (1) It is stress-free liquid electrode and mercury can be easily purified by distillation. (2) Solid electrode might form passive surface film which could prevent the contact between electrode and electrolyte. If a passive film is formed on the mercury surface, it can easily be broken by shaking. (3) Smooth surface is naturally formed on the mercury surface, unlike other solid metal surface such as Pt, of which a good smooth electrode surface must be obtained by heating.

The Concept of Kinetically Equilibrium Potential

The observed potential of an electrode is called by several names, open-circuited, rest or steady potential which is usually different from thermodynam-
二一 ically reversible potential. Several theories which attempt to explain the discrepancy of the rest potential from reversible potential have been proposed, such as mixed potential theory, chemical adsorption, poisons.[8,11] In the presents state, the discrepancy is still not satisfactorily explained.

In the investigation of these phenomena, closed homogeneous calls were used. The cells were discharged for a long time with the hope that certain equilibrium can reach for each electrode inside the cells. If one of the two electrodes is a reversible electrode such as hydrogen electrode using platinized Pt, the residual potential of the homogeneous cell is still not zero after exhaustively discharged, then the potential of other electrode is not thermodynamically reversible value. We call this potential as kinetically equilibrium potential (K.E.P.).

The reason we call this potential as kinetically equilibrium potential is that it can be derived kinetically as following: The Butler-Volmer equation for the following electrochemical reaction is

$$2H^+ + 2e^- \underset{K_b}{\overset{K_f}{\rightleftharpoons}} H_2 \qquad \text{at the platinized Pt}$$

$$i = 2FK_b C_{H_2} e^{2(1-\beta)FE/RT} - 2FK_f C^2_{H^+} e^{-2\beta FE/RT} \tag{1}$$

β is the transfer coefficient, i is current, E is potantal of the electrode.
At i=0 for open-circuited situation, we can derive the equation as,

$$E = \frac{RT}{2F} \ln \frac{K_f}{K_b} + \frac{RT}{2F} \ln \frac{C^2_{H^+}}{C_{H_2}} \tag{2}$$

Similarly, for the electrochemical reaction at the gold electrode, we have,

$$2H^+ + 2e^- \underset{K_{b'}}{\overset{K_{f'}}{\rightleftharpoons}} H_2 \qquad \text{at the gold electrode}$$

$$E' = \frac{RT}{2F} \ln \frac{K_{f'}}{K_{b'}} + \frac{RT}{2F} \ln \frac{C^2_{H^+}}{C_{H_2}} \tag{3}$$

For the situation of homogeneous cell consisting of a platinized and a gold electrode, as the cell reaches its internal equilibrium after long discharge time, the concentration of H^+ and H_2 are the same around both electrodes. The only difference is the forward rate constant K_f and backward rate constant K_b. It should be noted that the electrode kinetical equation (1) might be over-simplified for the hydrogen electrode, since there is other reaction such as recombination of hydrogen atoms. But it serves to show the idea to be developed here. 三

The difference of equations (2) and (3) is

$$\Delta E = E' - E = \frac{RT}{2F} \ln \frac{K_{f'}}{K_{b'}} - \frac{RT}{2F} \ln \frac{K_f}{K_b} \tag{4}$$

$$= \frac{RT}{2F} \ln Q'_k - \frac{RT}{2F} \ln Q_k = 300 \text{ mV at } 30°C$$

$$\frac{Qk'}{Qk} = 10^{10}$$

So the potential of Au which is different from the thermodynamically reversible potential of platinized platinum is due to the larger k quotient Q_k than that of platinum Q_k.

Experimental.

The apparatus used was the same as that described in the previous report[5] with slight modification. Since mercury is a liquid electrode, a proper amount of purified mercury could be placed in the bottom of the 4-necked 250 ml flask. The electric contact with the mercury was obtained by submersing a platinum-pointed end of a glass tube completely into mercury. The other end was fastened with a fine Pt wire to the coarse Pt which passed through a glass stopper in an outlet of the flask. Mercury instead of vaseline was used to cover up the flask outlet to prevent leakage.

In this experiment, because mercury was on the bottom of the flask, the solution was not stirred magnetically, but shaken occasionally. It was found, because of the liquid mercury electrode, the equilibration can be reached in a shorter time. The platinum used as electrode was also Marz grade (purity 99.99%) and heat-treated in the same manner as mentioned previously.[5] The reason for the heat treatment is that smooth Pt electrode obtained gives rise to higher positive potential and better reproducibility. The electrolytes HC1, HBr, H_2SO_4 were all analytical grade. The concentration of mercury ions after experiment was determined by atomic absorption and that of HC1, HBr, and H_2SO_4 were determined by acid-base titration.

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Results.

The homogeneous cells using mercury electrode are more difficult to investigate than homogeneous cells using copper or silver electrode, since the surface of platinum either bright or platinized could be wetted by mercury during discharging. It was found once the Pt electrode was slightly wetted with mercury, the residual potential dropped to a very small value. When this happen, the platinum electrode was withdrawn from the flask when hydrogen bubbling and washed with concentrated nitric acid, distilled water, and put back to the flask. The residual potential can be found restored to its original value.

(1) Homogeneous cells using hydrochloric acid (cell No. 1, No. 2 and No. 3)

If the bubbling of H_2 into the solution was carefully carried out and no oxygen left in the flask, then, there was no Hg_2Cl_2 produced on Hg surface at the early stage of discharging, the potential was measured to be very small about 0.008 volt (No. 3 in Table 1). After prolong discharge (about 30 days) until gray Hg_2Cl_2 was found sparsely covering mercury surface, the residual potential was measured to be 0.126 volt (cell No. 1 in Table 1). If the bubbling of H_2 into solution was not carefully carried out and some oxygen left in the flask, then some gray Hg_2Cl_2 produced on Hg surface due to oxidation, or if a small amount of $HgCl_2$ was introduced into the flask, the potential was immediately measured to be 0.130 volt. After prolong discharge for more than two weeks, the potential stayed at about 0.126 volt. Therefore the residual potential of cell No. 1 should be 0.126 volt. Due to variation of residual potential of four runs, the standard deviation of the residual potential was roughly estimated to be 0.030 volt. After the experiment, equilibrium concentration of mercury ion was determined to be 1.03×10^{-4} mole/liter. The concentration of HC1 was determined to be 0.417 N. The decrease of the concentration of HC1 from initial 0.465 N to 0.417 N was due to the loss of volatile HC1 during H_2 bubbling.

If platinized platinum was used instead of bright Pt, the residual potential found was as high as 0.290 volt with reverse polarity. The constant residual potential was found capable of maintaining about one week. The variation of the residual potential with temperature shows the decrease of residual potential with 五
increasing temperature.

(2) Homogeneous cells using hydrobromic acid (cell No. 4, No. 5 and No. 6)

The general features of cell No. 4 and cell No. 5 are quite similar to those of cell No. 1 and No. 2. Cell No. 6 was more difficult to be investigate than other cells, since the bright Pt in this cell was contaminated with Hg or HgO more easily during discharge than other cells. When contamination happened, its potential dropped. But the potential can be restored by washing the bright Pt with concentrated nitric acid. If no oxygen left inside flask after hydrogen bubbling, gray Hg_2Br_2 was not found over Hg at the earlier stage of discharge, at this time potential measured to be about 0.221 volt. (cell No.6). But after prolong discharging (50 days), Hg_2Br_2 was found to cover on the mercury surface, its residual potential was found to be 0.265 volt. Five runs have been done on cell No. 4, the standard deviation of residual potential was estimated to be about 0.040 volt. Instead of using bright Pt, platinized Pt was used, its emf was 0.125 volt with the polarity reversed. It was also found, the constantly residual potential can maintain for about one week.

(3) Homogeneous cells using sulfuric acid (cell No. 7 and No. 8)

In the previous cells, HC1 or HBr was used, in which halide ion can chemically react with mercury. In this cell, the sulfate ion can be considered to be inert to mercury. The residual potential of cell No. 7 is very small about 0.003 ± 0.001 volt. In this experiment, constantly residual potential was reached after 3 days of discharging. Instead of using bright Pt, platinized Pt was used in open circuit condition, the potential of cell No. 8 can maintain 0.530 volt for at least ten days. But if discharging cell the potential could gradually decrease to about 0.345 volt after another ten days.

Discussion and Conelusion

For the cell No. 3, the residual potential is 0.008 with bright Pt as the positive electrode. It can be considered that mercury and bright Pt electrodes have about the same K.E.P. . The difference of T.E.P. and K.E.P. between bright Pt and platinized Pt can be estimated from cell No. 2 and cell No. 3 as 0.298 volt as shown in Table 2. In the same way, we can estimate the K. E. P. of bright Pt in HBr and H_2SO_4. The results are shown in Table 2 along with the K.E.P. of mercury.

From the Table 2, we can see that anions influence the K.E.P. of mercury greatly. Sulfate ion is least reactive with mercury, while bromide ion is most reactive with mercury. The electrochemical reactions of mercury with $C1^-$ and Br^-

are as followings:

$$2\,Hg + 2\,Cl^- \rightleftharpoons Hg_2Cl_2 + 2\,e^- \qquad E^\circ = -0.2680\,v$$

$$E_1 = -0.268 + 0.060 \log a^2_{Cl^-} \qquad (5)$$

$$2Hg + 2\,Br^- \rightleftharpoons Hg_2Br_2 + 2\,e^- \qquad E^\circ = -0.139v$$

$$E_2 = -0.1392 + 0.060 \log a^2_{Br^-} \qquad (6)$$

Concentrations of Cl^- and Br^- are about the same in this experiment,

$$\triangle E = E_1 - E_2 = -0.1288 \qquad (7)$$

This value 0.1288 v is close to the difference of K.E.P. of mercury in HCl and HBr, i.e., 0.290-0.125=0.165 v.

Sulfate ion can be regarded as non-reactive with Hg, but Cl^- is reactive with Hg with $E^\circ = -0.268$ v which is close to the difference of mercury K.E.P. in HCl and H_2SO_4, i.e. 0.290-0.530 = -0.240 v. These comparisons are meaningful, since they show that the hydrogen electrode with substrate metal Hg is influenced by anion Cl^- or Br^- to the same degree as shown by their electromotive forces. They decrease K.E.P. and bring the electrode potential closer to the T.E.P..

It is very interesting that when mercury is not covered by Hg_2Cl_2, the potential is quite low about 0.008 v (cell No. 3). This kind of state can persist quite long time. In this state, the mercury electrode Hg / Cl^- is known as an ideally polarizable electrode as mentioned by Grahame.[12] It is a highly irreversible electrode possible with a high positive interfacial potential (potential of solution is taken as zero) for the H_2-H^+ equilibrium. Bright platinum electrode with its positive zcp (zero charge potential) about 0.17 v[13] should have positive interfacial potential. Therefore, their net potential is quite small as expected. The small residual potential of cell No. 7 can also be explained by the same reasons.

By prolong discharge or by introducing Hg_2Cl_2 into the flask and there was Hg_2Cl_2 sparely covering on mercury electrode, the residual potential is 0.126 volt. This is because that in the presence of Hg_2Cl_2, the electrochemical reaction of the mercury electrode can be expressed as 七

$$2\,Hg + 2\,Cl^- \rightleftharpoons Hg_2Cl_2 + 2\,e^-$$

also because of highly reversible nature of this electrochemical equilibrium, it is easy for charge to leak through the interface and substantial charge build-up on electrode and solution side is impossible. Therefore, it is expected that interfacial potential of this calomel electrode is small as compared with that of bright Pt in the cell No. 1. So net potential (residual potential) is expected to be large about 0.126 v. Cell No. 4 can also be explained by similar reasons. The difference of the metal-solution interfacial potential distribution of Hg | Hg_2Cl_2 and Pt as in cell No. 1 is shown in Fig. 1. Its residual potential is $\triangle \phi$ which should be permanent and assumed a non-zero value, since the structure of the electric double layers are usually different for different metal electrodes even in equilibrium. It must be emphasized that by this viewpoint, an inevitable conclusion is that there should be non-zero residual potential of the most homogencous cells as experimentally found.

By using stress-free liquid mercury electrode, it was thought that the equilibrium could reach in a shorter time and finally the residual potential reached zero. Although it took shorter equilibrium time, the residual potentials were found not to be zero. the nonzero reisdual potential of the homogeneous cells investigated here is still not easily explained. One possible explanation for the non-zero residual potential of cell No. 1 and No. 4 is the cyclic mechanism, that is,

$$2\,Hg + 2\,X^- \rightarrow Hg_2X_2 + 2\,e^- \text{ at the Hg electrode} \qquad (8)$$

$$2\,H^+ + 2\,e^- \rightarrow H_2 \qquad \text{at the Pt electrode} \qquad (9)$$

$$Hg_2X_2 + H_2 \rightarrow 2\,Hg + 2\,HX \qquad (10)$$

$$X = Cl^- \text{ or } Br^-$$

The last chemical reaction (10) is for recovery to its original state. The different K.E.P. of Hg shown in Table 2 might be due to the different electrode potential of reaction (8). The cyclic mechanism of H_2-H^+ electrochemical conversion can also be proposed for the cell No. 2, 5 and 8 as in the previous report.[5] These explanations undoubtedly violate the second laws of thermodynamics and principle of microrversibility.

MacGillavry[14] has investigated the potential of nickel in nickel-free hydroxide and phosphate solution. He found that the steady potentials did not obey the Nernst equation. He concluded that the Nernst equation was only applicable to reversible electrode. Results of this experiments seem to support his conclusion. Because if Nernst equation is valid, we can show that there should no residual potentials of these homogeneous cells. Brenner[15] investigated the enthalpy change of liquid-liquid junction potentials and concentration cells and found that Gibbs-Helmholtz equation was not obeyed. Recently Howard Johnson[16] demonstrated a perpetual motion of magnet-powered motor. If the perpetual motion machine is possible, why not the possibility of the perpetual electrochemical cells with cyclic mechanism proposed in this report. More studies either theoretical or experimental should be done on this important aspect of electrochemistry.

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Table I, Experimental results of the homogeneous cells at 30°C under H_2 atmosphere (1 atm)

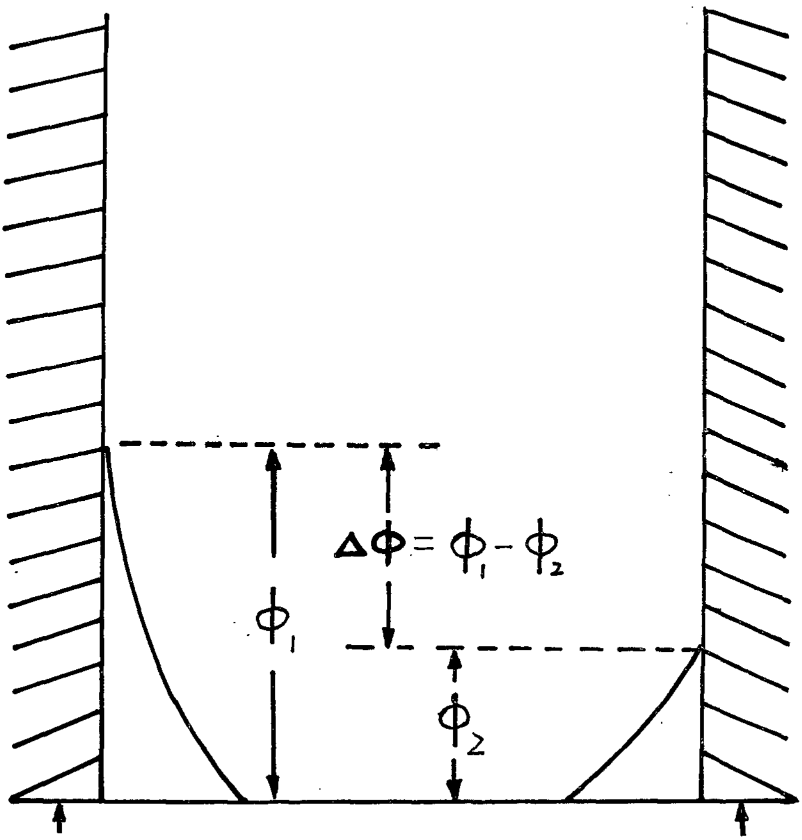
Cell No.	Homogeneous cell	Concentration of electrolyte determined after each experiment	Equilibrium conc. of mercury ion (mole/liter)	Residual potential (volt)
1	$Hg, Hg_2Cl_2 \mid HCl\ (0.465N) \mid Pt^{\oplus\star}$ (b)★★	HCl (0.417N)	1.03×10^{-4}	0.126 ± 0.030
2	$Hg^{\oplus} \mid HCl\ (0.462N) \mid Pt$ (P)	HCl (0.421N)	0.205×10^{-4}	-0.290 ± 0.040
3	$Hg \mid HCl\ (0.462N) \mid Pt^{\oplus}$ (b)	HCl (0.420M)	0.503×10^{-4}	0.008 ± 0.004
4	$Hg, Hg_2Br_2 \mid HBr\ (0.492N) \mid Pt^{\oplus}$ (b)	HBr (0.440N)	1.85×10^{-3}	0.265 ± 0.040
5	$Hg^{\oplus} \mid HBr\ (0.492N) \mid Pt$ (P)	HBr (0.435N)	0.488×10^{-4}	-0.125 ± 0.030
6	$Hg \mid HBr\ (0.492N \mid Pt^{\oplus}$ (b)	HBr (0.440N)	3.81×10^{-4}	0.221 ± 0.040
7	$Hg \mid H_2SO_4\ (0.512N) \mid Pt^{\oplus}$ (b)	H_2SO_4 (0.494N)	2.61×10^{-5}	0.221 ± 0.001
8	$Hg^{\oplus} \mid H_2SO_4\ (0.512N) \mid Pt$ (p)	H_2SO_4 (0.495N)	6.51×10^{-5}	-0.530 ± 0.040

★ ⊕ indicates the positive electrode;

★★ (b) indicates that Pt is bright electrode; (p) the platinised Pt

Table 2 K. E. P. of Hydrogen Electrodes relative to Platinized Pt

Substrate Metal used	Electrolyte used	K. E. P. at 30°C
Pt (bright)	HCl	0.298 v
Hg	HCl	0.290 v
Pt (bright)	HBr	0.346 v
Hg	HBr	0.125 v
Pt (bright)	H_2SO_4	0.526 v
Hg	H_2SO_4	0.530 v



Irreversible Electrode such as Pt (bright) or Au

Reversible Electrode such as $Hg|Hg_2Cl_2$

Fig. 1 Sketch of Potential Distribution of Reversible and Irreversible Electrode. ϕ is metal-solution Interfacial Potential of Electrode.

均匀電池中汞及鉑電極之動力平衡電位之研究

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中文摘要

吾人曾研究具有汞及鉑電極的均匀電池。原先認爲利用無應力的液態汞電極，這些均匀電池之剩餘電壓應短時間達成平衡，但實驗結果顯示雖然達成平衡時間爲短，但剩餘電壓並不爲零。在此文中，也引進動力平衡電位的新觀念。另外既使在平衡下，從不同電極的不同電雙層構造之關係來看，大都份的剩餘電壓不應爲零，此與實驗結果吻合。