HYDROGEN EVOLUTION REACTION ON
GOLD-MERCURY ALLOYS OF
VARIOUS COMPOSITION

By

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Abstract

The hydrogen evolution reaction (H. E. R.) was studied on Au–Hg alloy electrodes of various compositions in 1N H₂SO₄ solution at room temperature. Au and Hg were selected as representing the d- and sp-metals, where the d-metals (transition and IB metals) are essentially different from the sp-metals (metals after IIB) in H. E. R. and electroreduction of organic compounds.

Alloys of 0.049, 0.10, 0.12 and 0.13 wt. % Au show the same catalytic activity for H. E. R. as Hg, suggesting that the catalytic activity of Au disappears when it is atomically dispersed. Two-phase alloy of Au₂Hg₃ and AuHg₂ shows almost the same activity as Au. This fact indicates that the mercury in the form of intermetallic compounds, Au₂Hg₃ and AuHg₂, does not poison the catalytic activity of Au. A change of the activity of Au will be expected after the addition of more than 67 wt. % Hg.

I. Introduction

One of the present authors (H. K.) surveyed the catalytic activity for the hydrogen electrode reaction,¹ and the selectivity in electroreduction of organic substances² at various electrode metals. He concluded that the family of metals is divided into two groups. One of them is the transition and IB metals (called d-metals) and the other is the metals after IIB in the periodic table (called sp-metals). Electrocatalyses on the former group of metals seem to occur basically via “non-polar” process, while on the latter via “polar” process, respectively.² The author explained many phenomena observed with respect to the hydrogen electrode reaction on the basis of the catalytic and electrochemical mechanisms for the d- and sp-metals, respectively.¹ Rate-determining steps of the respective mechanisms are the recombination of

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adsorbed hydrogen atoms and the discharge of an adsorbed hydrogen-molecule ion, \(H_2(a)\), where the former will be the “non-polar” process, while the latter the “polar” process. It is also concluded that the factor of primary importance in the determination of catalytic activity is a physical property of metal and that the surface state or the solution composition is the secondary factor. The purpose of the present paper is to clarify the relation between the catalytic activity and the composition of the alloy which consists of Au and Hg, each of these metals representing the \(d\)- and \(sp\)-metals, respectively.

Many experiments have been reported on the hydrogen electrode reaction at alloy electrodes. (i) The relation between the catalytic activity and electronic structure, especially \(d\) \% character, has been studied on the system Ni–Cu,\(^{3,4}\) Au–Pd,\(^{5,6,7}\) and Rh–Pd.\(^{8}\) In these systems, the alloys used are made from the metals of the \(d\)-metals. (ii) The alloys of the \(sp\)-metals were also studied on the systems, Hg–In,\(^{9,10}\) Hg–Tl,\(^{11}\) and Ga–In–Hg.\(^{12}\) (iii) The effect of electron concentration of alloys on the catalytic activity has been studied on the systems, Cu–Sb, –Sn, –Al, –In, –Zn, –Ni,\(^{13}\) Ag–Cd, –In, –Sn, –Sb,\(^{14}\) Au–Zn, –Cd, –In, –Sn,\(^{15}\) and Cu–Al, –Ga, –Ge, –As.\(^{16}\) (iv) The alloys, Ni–As, –Sb, –Te, –S\(^{17}\) have been also studied.

Butler and Makrides studied the effect of aggregation of metal atoms on the catalytic activity by using the systems, Hg–Pd and Hg–Pt.\(^{18}\) They concluded that atomically dispersed Pd or Pt lose their activity observed at the bulk state. Giles et al.\(^{19}\) examined the activity of Pt and Ru deposited on graphite electrode in controlled amounts and discussed the role of edge and plane of the deposit.

In the present study, the Au–Hg system was examined. Hg is known to be much less active compared to Au. In addition, according to the conclusion of the present author (H. K.),\(^{1,2}\) IB metals behave essentially in a similar way to transition metals, though their catalytic activity is about \(10^3\) times at most smaller than that of the latter. On the other hand, the electrochemical behaviour of IIB metals is essentially different from IB metals and the catalytic activity is further lowered by ca. \(10^6\) times in comparison with IB metals. Hence, it is of interest to study the catalytic activity of the alloy composed of IB and IIB metals as a function of their composition. Among IB and IIB metals, Au and Hg were selected because of their stability against the oxidation of the surface.

II. Experimental

Material; Hydrogen from cylinder was purified by the purifier, LW-06SC, Japan Pure Hydrogen Co. Inc., Japan. Surphuric acid was of special
grade and was used without further purification. Electrolyte was prepared by using conductivity water. Mercury was purified by air oxidation in 5% HNO₃ solution and then by triple distillation in vacuum. Spectroscopic analysis showed that the mercury thus prepared has a purity of 99.999%. Gold wire (dia. 0.1 mm) was supplied from Johnson-Matthey Co., London and was of purity of 99.999%.

**Cell:** A cell of the three-compartment type was used in the case of measurements on wire electrode, i.e., the cell consisted of the reference, test and counter electrode compartments. Measurements on the hanging electrode were carried out in another cell consisting of the reference electrode compartment and the main compartment with water-jacket. The test electrode and main compartments of the respective cells could hold several electrodes movable up and down by means of slip joints in the top of the cap. All the taps of the cells were water sealed. Details of the cell have been described elsewhere.²⁰,²¹

**Electrode:** The reference and counter electrodes were platinized platinum wire and gauze, respectively. The test electrodes were prepared as follows. (i) Hg; Hanging drop of mercury was used as electrode (surface area was 0.025 cm²). (ii) Hg-rich electrode; Hg-rich alloys were prepared by heating the mixture of Hg and Au at 0.05, 0.1, 0.5, and 1 wt. Au % in quartz vessel in hydrogen atmosphere of 1 cm Hg at 250°C. The vessel was shaken for at least one month. Alloy composition was then determined by the Rhodamine B method.²² Results were 0.049, 0.10, 0.12, and 0.13 wt. Au % for respective mixtures. Solubility of Au in Hg is reported as 0.1306 wt. Au % at room temperature. Hence, these alloys are taken to be solid solutions. These alloys were used in the form of hanging drop as electrode. Surface area was 0.027 cm². (iii) Au-rich electrode; Au-rich alloy was prepared by heating gold wire of several meters in quartz vessel which contained a drop of mercury of 0.1 g at the bottom. The vessel was kept at 600°C for about three months except for the bottom part which was kept at 300°C. Hydrogen of 1 cm Hg was introduced to prevent the oxidation of surface. The composition of the alloy thus prepared was 81 wt. Au % by the Rhodamine B method. X-ray study, however, showed that the surface layer consisted of two phases, Au₃Hg₅ and AuHg₂, without the indication of free Au and Hg. The electrode was prepared by cutting this wire at 2 cm in length and spot-welding to Pt wire which was sealed into glass tube. The part of the welding and Pt wire exposed were covered with Araldite. Apparent surface area was 0.063 cm². (iv) Au; A wire of 2 cm in length (Apparent surface area, 0.063 cm²) was connected to Pt wire as
stated above and served as electrode. The electrode was cleaned with benzene, alcohol and then washed with the conductivity water.

**Procedure:** Cell was cleaned with conc. $\text{H}_2\text{SO}_4-\text{HNO}_3$ mixture for overnight and rinsed thoroughly with the conductivity water. After setting wire electrodes or the capillary for dropping mercury, spoon and glass tube for hanging a mercury drop, the cell was introduced to the apparatus. An electrolyte solution of $1\text{N H}_2\text{SO}_4$ was introduced to the cell by application of hydrogen pressure and was pre-electrolyzed with a current of a few mA overnight under bubbling of hydrogen. Pre-electrolysis was stopped by pulling the electrode for pre-electrolysis out of the solution. The hanging drop electrode was prepared by transferring a drop by spoon from the capillary to the glass tube, at the end of which the cross section of Pt wire (dia. 0.3 mm) was exposed. Measurements were carried out by the galvanostatic pulse method. Potential change of the electrode was followed by cathode ray oscilloscope. The steady value of the potential was taken as the overvoltage.

![Fig. 1. Tafel lines on Hg.](image)

1; Present result ($0.95 \text{N H}_2\text{SO}_4, 25^\circ\text{C}$), 2; BETHUNE ($1\text{N HCl, 25^\circC}$), 3; POST and HISKEY ($0.1\text{N HCl, 21^\circC}$), 4; BOCKERIS and AZZAM ($5\text{N HCl, 25^\circC}$), 5; BUTLER and MAKRIDES ($0.1\text{N HClO}_4$), 6; CONWAY and SALMON ($1\text{N HCl-CH}_3\text{OH, 27^\circC}$), 7; NAGASHIMA and KITA ($1\text{N H}_2\text{SO}_4, 25^\circ\text{C}$).
after correction of IR drop. Measurements on the wire electrodes were conducted at room temperature but those on the hanging drop electrodes were at 25.0±0.1°C.

III. Results and discussion

III-1 Hg

The Tafel line observed on the hanging drop of Hg at 25.0°C in 0.95N H₂SO₄ solution is expressed as,

\[ \eta(V) = 1.245 + 0.0845 \log i, \]  

as the mean of eleven runs where \( i \) denotes the current density in A/cm² and \( \eta \) the overvoltage, respectively. The above equation is compared with the reported results \(^{18,24-28}\) in Fig. 1. The Tafel slope of the present work is slightly smaller than the reported ones.

III-2 Au

(i) Unactivated electrode; The Tafel line on Au wire electrode varies

![Graph](image-url)

\( \eta \) vs \( \log i \) on Au electrodes in 1.1 N H₂SO₄ at room temperature. Solid line represents the Tafel line estimated from the results at \( \log i (A/cm²) < -0.2 \) by the least square mean method. Different symbols refer to different runs. Dotted line shows the Tafel plot observed immediately after the activation of electrode by the anodic polarization with \( i = 1.7 \text{ mA/cm}² \).
to a great extent. Figure 2 shows typical results observed on seven electrodes in 1.1N H₂SO₄ solution at room temperature. The overvoltage at, for example, 0.1 A/cm² fluctuates from 0.38 to 0.52 V. The Tafel line obtained by the least square mean method is,

$$\eta(V) = 0.589 + 0.137 \log i \quad (2)$$

The above equation is compared with the reported results⁵,²⁹⁻³⁹ in Fig. 3. Au is one of the metals on which the results are widely divergent.¹,² The present result is located in the mean position.

![Fig. 3. Tafel lines on Au.](image)

1; Present result (1.1 N H₂SO₄, room temp.), 2; HICKLING and SALT⁵⁰ (1 N HCl, 17°C), 3; BOCKRIS and PARSONS⁵⁰ (1 N HCl, 20°C), 4; Ives and SWAROOPA,¹¹ Ives¹² (0.1 N HCl), 5; BREITER, KAMMERMAIER and KNORR⁵¹ (8 N H₂SO₄, room temp.), 6; PENTLAND, BOCKRIS and SHELDON⁴⁹ (0.1 N HCl, 25°C), 7; SCHULDINER and HOARE⁵¹ (2 N H₂SO₄, 25°C), 8; AMMAR and RIAD⁵¹ (Au–Cu Alloy (Cu, 0.5%), 0.1 N HCl, 30°C), 9; idem⁵¹ (Au–Cu Alloy (Cu, 0.5%), 0.1 N HCl, 30°C), 10; CONWAY⁵¹ (0.1 N HCl, 25°C), 11; GOSSNER and LOEFFLER¹⁷ (2 N H₂SO₄, 20°C), 12; SCHMID¹⁸ (1 N HClO₄, 20°C), 13; KUHN and BYRNE¹⁸ (1 N H₂SO₄, 20°C).

(ii) Activated electrode; An attempt was made to obtain a reproducible result by anodic pre-treatment of the electrode. A typical galvanostatic transient at anodic polarization is shown in Fig. 4. The decay curve of the transient clearly indicates the presence of two states of surface oxide. The sharp drop of the potential to the original value suggests the disappearance of the surface oxide. The Tafel line observed immediately after the disappearance of the surface oxide is shown in Fig. 2 by the dotted line. Over-
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**Fig. 4.** Anodic transient on Au in 1.1 N H₂SO₄ with a current density of 1.7 mA/cm².

**Fig. 5.** Time dependence of the overvoltage of the activated Au electrode in 1.1 N H₂SO₄. Measurements were carried out with the short pulse of \( i = 0.175 \) A/cm² at time, \( t \) after the activation. Curve 1: \( \eta \) vs \( \sqrt{T} \), Curve 2: \( \eta \) vs \( t \).
voltage decreases to a very small value, e.g., from 0.45 to 0.08 V at 0.1 A/cm², but increases gradually with time, t. Figure 5 shows the time dependence of the overvoltage at a current density of 0.175 A/cm². The overvoltage increases linearly with $\sqrt{t}$ during the first 1 hr (curve 1), while later on linearly to $t$ (curve 2). After 24 hr., the overvoltage approaches the value before activation. Such a time dependence of the overvoltage after the activation makes it difficult to determine the intrinsic value of the catalytic activity for gold. Hence, the catalytic activity of gold was determined from Eq. (2).

Differential capacity of the electrode was also followed after the activation. Results are illustrated in Fig. 6, where the differential capacity was obtained from the initial slope of the galvanostatic transient and the current density used. The differential capacity increases by three times by the activation and then decreases gradually, though its value after 24 hr. is still larger by ca. 2 times than that of the unactivated electrode.

Possible causes for the time dependence of overvoltage may be the reorientation of surface metal atoms or impurity adsorption from solution. A recent study carried out in author’s laboratory showed that the overvoltage change on Pt electrode is independent of the kind of acidic electrolyte solu-
Hence, the reorientation of the surface metal atoms will be most likely responsible for the overvoltage change of the activated electrode. Quantitative explanation for the time dependence will require further detailed information.

III-3 Au-Hg Alloys

(i) Hg-rich system; Figure 7 shows the Tafel lines as the mean of 10, 12, 23 and 3 runs obtained on 0.049, 0.10, 0.12 and 0.13 wt. Au % alloy electrodes in 0.96N H₂SO₄, respectively. Tafel equations are:

Fig. 7. Tafel lines on Hg–Au alloy electrodes in 0.96 N H₂SO₄.

Comparison of these results with that on Hg, i.e., with Eq. (1), indicates no effect of gold in the alloys on the Tafel line.

It must be mentioned, however, that the alloy composition may be different at the surface and the gold content be extremely small in comparison...
with the bulk composition. Thus, the Tafel line was observed in 1N H₂SO₄ solution which contains auric ion of a concentration of \(2.92 \times 10^{-4}\) mole/l, so that gold can codeposit on the surface with hydrogen. Limiting current for the diffusion of auric ion of this concentration was estimated as 3.2 \(\mu\)A from the polarogram, which results in the deposition of \(2 \times 10^{14}\) gold atoms per sec per cm². Curve 1 of Fig. 8 shows the Tafel lines observed in the

![Fig. 8](image)

**Fig. 8.** Curve 1: The Tafel line on Hg in 1.0 N H₂SO₄ (○) and in 1.0 N H₂SO₄ + 2.92 \(\times\) 10\(^{-4}\) mole/l Au\(^{3+}\) solutions (●). Curve 2: The Tafel line on Hg–Au alloy of which surface layer consists of Au₂Hg₃ and AuHg₂ (three runs).

absence (○) and presence (●) of auric ion. Any significant effect of the deposited gold atoms on the Tafel line is not detected. Since the Tafel line was observed by the galvanostatic pulse of which duration is between 0.01 and 0.1 sec, the amount of gold deposited is between \(2 \times 10^{12}\) and \(2 \times 10^{13}\) atoms/cm². Thus, the above results indicated that the presence of gold atoms in the surface up to 0.2~2% at maximum does not affect the Tafel line, supporting the results obtained on Hg-rich alloys.

(ii) Au-rich system; The Tafel line on the Au-rich electrode is expressed as
\[ \eta(V) = 0.59 + 0.118 \log i \]  

(7)

and is represented by curve 2 in Fig. 8. Comparison of this result with that of gold, i.e., with Eq. (2), shows essentially no difference in the Tafel line between them. Difference in the value of the Tafel slope will not reflect any significant mean because of the poor reproducibility of the results on Au.

### III-4 Comparison of the Catalytic activity

The exchange current density, defined as unidirectional current density at equilibrium, is given from the Tafel line as

\[ \log i_0 = -a/b, \]  

(8)

where \( a \) is the overvoltage at 1 A/cm\(^2\) and \( b \) the slope of the Tafel line. Since the more active the electrode is, the larger the exchange current density is, the latter will be taken as a measure of the catalytic activity of the electrode. Figure 9 shows the value of \( \log i_0 \) on the respective electrodes studied. The phase diagram is also illustrated with a dotted line in Fig. 9.

![Fig. 9. \( \log i_0 \) vs the composition of Hg-Au alloy electrodes in 1N H\(_2\)SO\(_4\). Dotted lines illustrate the phase diagram of Hg-Au alloy.](image)

The catalytic activity of Au is about \( 10^6 \) times larger than that of Hg. If the catalytic activity of Au is assumed to be divided into individual surface atoms, the alloy of 0.10 wt. Au % would show the catalytic activity about \( 10^3 \) times less than Au itself but about \( 10^3 \) times larger than Hg. The catalytic activities observed on 0.049, 0.10, 0.12 and 0.13 wt. Au % alloy
electrodes, however, are almost the same as that of Hg. Hence, the following conclusion will be drawn; The catalytic activity of Au disappears when it is dispersed to an atomic level. The same conclusion has been reported by BUTLER and MAKRIDES on Hg–Pd and –Pt systems. In the case of the Mg–Hg system, however, it is well known that the deposition of Mg decreases the hydrogen overvoltage to an appreciable extent. The present conclusion might not be applicable to this system.

On the other hand, the catalytic activity of the alloy of ca. 60 wt. Hg % is almost the same as that of Au itself. It is of interest to note that though Hg is well known as a strong poisoner in most catalyses, the presence of Hg in the forms of AuHg3 and AuHg2, does not change the catalytic activity at all. A sharp change in the catalytic activity will then be expected at the composition above ca. 67 wt. Hg %. ENGEL reported that the properties and alloy behaviour of the IB metals are better accounted for if the filling of the d-shell is placed between Cu and Zn, Ag and Cd, or Au and Hg leaving Cu, Ag and Au as transition metals. Pauling has proposed a value of 5.44 for the metallic valence of IB metals. It has also been pointed out that Pauling’s value instead of monovalence gives much better result in calculation of the electronegativity by Gordy’s equation. The present author classified IB metals as the d-metals from the experimental facts on many electrocatalyses as stated in the Introduction. Thus, it might be expected that the d-shell of Au will be filled at the composition above ca. 67 wt. Hg % alloy, though copper, for example, has been considered a one electron metal with a filled d-shell.

IV. Summary

1. The hydrogen evolution reaction has been studied on Hg, Au and their alloys of various composition in 1N H2SO4 solution at room temperature.
2. The alloys of 0.049, 0.10, 0.12 and 0.13 wt. Au % show the same catalytic activity for the reaction as Hg. This fact leads us to conclude that the catalytic activity of gold disappears when it is dispersed into atoms.
3. The alloy consisting of two phases of Au2Hg3 and AuHg2 shows almost the same activity as gold. It is of interest that this behavior is completely unexpected from the well-known poisoning action of Hg. A sharp change in the catalytic activity will be expected at the composition above ca. 67 wt. Hg %.
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