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# SEPARATION FACTOR OF DEUTERIUM ON PLATINUM HYDROGEN ELECTRODE IN AQUEOUS SULFURIC ACID

By

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## Summary

Electrolytic separation factor of deuterium on platinum hydrogen electrode in 1.34 N H<sub>2</sub>SO<sub>4</sub> containing 8.49 atomic percent deuterium was observed in hydrogen atmosphere of 12 cmHg total pressure at 15°C and different hydrogen overvoltages ranging from 0.02 to 0.55 volt. Thorough vacuum operations were applied to the observation as well as the preparation and purification of materials, the preelectrolysis of the above mentioned aqueous electrolyte and the cleaning of vessels and electrolytic cell used.

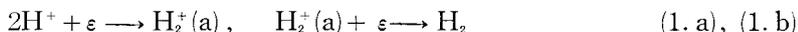
The separation factor was determined by measuring the deuterium content of the aqueous electrolyte and that of the hydrogen gas steadily electrolyzed at each constant overvoltage. It was demonstrated that the separation of deuterium thus observed was caused by genuine electrochemical reaction on the electrode surface but not by some transport process, *i.e.* the diffusion of hydrogen molecules in the aqueous electrolyte or the evaporation of the electrolyzed hydrogen gas or the diffusion of hydrogen ion. Separation factor was worked out from the observation by an equation, which was derived allowing for the reverse transfer of protium and deuterium for the limiting case of infinitely low deuterium content and demonstrated practically exact, as it is, under the present experimental condition of finite deuterium content.

The separation factor thus determined was found to increase from *ca.* 3.6 at zero overvoltage to a maximum value *ca.* 6.8 around 0.23 volt overvoltage and then slowly decreased down to 6.2 at 0.55 volt overvoltage. The observed initial increase verified the conclusion from the theoretical prediction of HORIUTI<sup>1,2)</sup> that the mechanism of hydrogen electrode reaction switches over from the electrochemical to the catalytic mechanism with increase of overvoltage along with the switch of separation factor from the characteristic value *ca.* 3 of the former mechanism to that *ca.* 7 of the latter one.

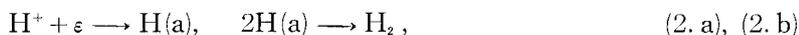
## Introduction

One of the present authors deduced theoretically in a previous paper<sup>1,2)</sup> that the hydrogen electrode reaction in aqueous electrolyte proceeds through either the electrochemical or the catalytic mechanism according to the condition of electrolysis defined by work function of the electrode, hydrogen pressure around the electrode, pH of the aqueous electrolyte and hydrogen overvoltage.

In the electrochemical, mechanism, the hydrogen electrode reaction is completed by the two steps<sup>\*2)-4)</sup>



with the rate governed by the latter one, where  $\text{H}_2^+(\text{a})$  is the hydrogen-molecule adsorbed on the electrode and  $\varepsilon$  the metal electron. The catalytic mechanism consists of the two steps<sup>2)3)5)6)</sup>



*i. e.* the neutralization of hydrogen ion to form the adsorbed hydrogen atom  $\text{H}(\text{a})$  and the recombination of the two  $\text{H}(\text{a})$ 's, which governs the rate.

It was thus shown<sup>1)2)</sup> that the mechanism may switch over from one to another along with the variation of overvoltage even on the same electrode in the same aqueous electrolyte. With special reference to the platinum hydrogen electrode, it was deduced<sup>1)2)</sup> that the electrochemical mechanism may be operative in the neighbourhood of the reversible hydrogen electrode potential (termed simply the reversible potential in what follows) at ordinary temperature and pressure under the condition  $\theta(\text{H}_2^+)\theta(0) \gg \theta(\text{H}^+)\theta(\text{H})$ , because of the extraordinary large work function of platinum, where  $\theta(\text{H}_2^+)$ ,  $\theta(\text{H}^+)$  and  $\theta(\text{H})$  are coverages of the electrode surface respectively by  $\text{H}_2^+(\text{a})$ ,  $\text{H}^+(\text{a})$  and  $\text{H}(\text{a})$ , and  $\theta(0)$  is the fraction of the bare surface. The theory predicts now that the electrochemical mechanism switches over, with increase of overvoltage (the excess of the reversible potential over the applied potential), to the catalytic mechanism but further increase of overvoltage restores the electrochemical mechanism.

Experimentally it was found by HORIUTI and OKAMOTO<sup>3)</sup> in 1N  $\text{H}_2\text{SO}_4$  at 0.3 volt overvoltage and room temperature, that the separation factors on different cathodes separate into two groups, *i. e.* that of the values *ca.* 3 and the other of the values *ca.* 7. This result was confirmed by an exhaustive experiment of WALTON and WOLFENDEN<sup>7)</sup>. The platinum electrode gave now the separation factor *ca.* 7 under the latter experimental condition. The theoretical calculation showed on the other hand that the electrochemical<sup>4)</sup> or the catalytic mechanism<sup>5)8)</sup> should give the separation factor *ca.* 3 or 7 respectively, whereas the slow discharge mechanism does a separation factor at least 12<sup>9)</sup>. It follows that the

\* ) HORIUTI and OKAMOTO (Ref. 3) advanced previously, as the electrochemical mechanism, step (2. a) followed by the rate-determining one  $\text{H}(\text{a}) + \text{H}^+ + \varepsilon \rightarrow \text{H}_2$ . It was shown later theoretically (Ref. 4) that the constituents  $\text{H}(\text{a})$  and  $\text{H}^+$  of the initial complex are combined readily and quite stably in  $\text{H}_2^+(\text{a})$  which led HORIUTI, KEII and HIROTA (Ref. 4) to revise the electrochemical mechanism as stated in the text. It is however open to question, whether the formation of  $\text{H}_2^+(\text{a})$  consists actually in a single step as conveniently expressed by (1. a) or else in more than one step.

hydrogen electrode reactions of the first and the second groups proceed necessarily through the electrochemical and the catalytic mechanism respectively and the mechanism of the platinum hydrogen electrode under the latter condition must be catalytic, provided that the above three mechanisms are all possible ones.

HORIUTI and IKUSIMA<sup>10)</sup> investigated on the other hand the mechanism of the hydrogen electrode reaction of platinum at lower overvoltage. They have observed the stoichiometric number  $\nu_r$  of the rate-determining step at unity, a pronounced dependence of the exchange current on pH and the characteristic dependence of current on overvoltage of the electrochemical mechanism<sup>10)\*</sup>. These results led them<sup>10)</sup> to conclude the electrochemical mechanism as operative at the low overvoltage. This conclusion as well as the experimental fact<sup>3)</sup> of the separation factor 7 at 0.3 volt overvoltage fits in with the above theoretical deduction and hence leads one to predict that the separation factor on platinum hydrogen electrode is near 3 around the reversible potential but increases with increase of overvoltage up to a maximum value *ca.* 7 and then decreases toward *ca.* 3 with further increase of overvoltage. The present work is devoted to the experimental verification of the above theoretical prediction.

A number of workers<sup>3)7)11)-13)</sup> observed the separation factor of deuterium, but their results deviate considerably from each other and those even of one and the same worker markedly fluctuate. This difficulty might be due to a gradual contamination of the test electrode with impurities along with the continuation of the electrolysis, which might possibly be eliminated by purifying the test cathode, electrolyte and the vessels and by preventing them from contamination by means of thorough vacuum operations. BOCKRIS<sup>14)</sup> has advanced an efficacious method of purifying aqueous electrolyte by preelectrolysis, which was, however, applied to the measurement of separation factor only by ROME and HISKEY<sup>12)</sup> and HISANO *et al.*<sup>13)</sup>, whereas none of the workers<sup>3)7)11)-13)</sup> conducted the experiment by thorough vacuum operations.

The present authors conducted the preelectrolysis and every other procedure systematically by vacuum operations to observe the separation factor as a function of the overvoltage ranging from 0.02 to 0.55 volt in 1.34 N H<sub>2</sub>SO<sub>4</sub> containing 8.49 atomic percent deuterium at 15°C.

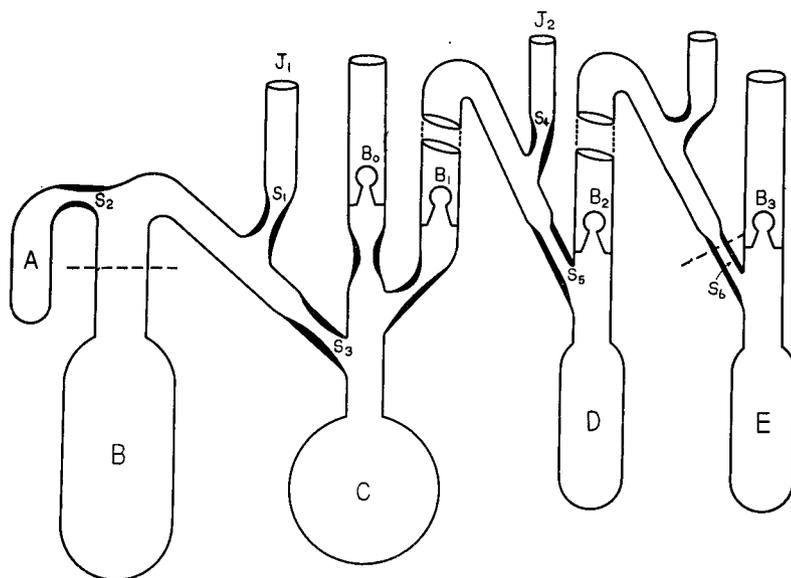
## § 1. Aqueous Electrolyte

The aqueous electrolyte, *i.e.* 1.34N H<sub>2</sub>SO<sub>4</sub> containing 8.49 atomic percent deuterium was prepared from sulfuric anhydride and heavy water. This procedure was preferred for the sake of expedient purification and determination of the deuterium content of the aqueous

\*) The TAFEL's constant  $(RT/F)\partial \ln i/\partial \eta$  is a constant proper fraction  $\alpha$  or  $1+\alpha$  respectively above or below a certain overvoltage, where  $i$  is the current density and  $\eta$  the overvoltage.

electrolyte. The sulfuric anhydride and the heavy water were purified separately and mixed together by vacuum operations as described in what follows.

All the vessels used in the present work inclusive of the electrolytic cell were made of "Hario" glass<sup>\*)</sup> supplied by SHIBATA & Co, Tokio. Each of the former vessels was filled with chromic acid mixture, kept thus in boiling water for several hours and then left standing overnight at room temperature. The vessel was then rinsed repeatedly with distilled water<sup>\*\*)</sup> until the acidity of the wash vanished, filled with distilled water and placed in boiling water several hours, the distilled water being renewed meanwhile several times. The vessel was fused to a vacuum line, as it was wet, by blowing the junction through a trap immersed in liquid nitrogen, and a greaseless tap, and then evacuated through the same trap and tap to dry it.



**Fig. 1.** Apparatus for  $\text{SO}_3$  purification.

$S_1, S_2 \dots S_6$ : constrictions.

$B_0, B_1, B_2, B_3$ : breakable joints.

$J_1, J_2$ : junctions to vacuum line.

Sulfuric anhydride was prepared by an apparatus shown in Fig. 1. Vessels B and C combined with each other were cleaned as above, fused to the vacuum line at  $J_1$ , dried by evacuation, air was admitted through the trap, B was cut off at the broken line, "the first class reagent" of 50% fuming sulfuric acid preliminarily liquefied by warming was poured into B, the content was frozen by liquid nitrogen, B was promptly replaced by fusing the cut and evacuated.

<sup>\*)</sup> Glass of the quality equal to pyrex glass according to the data given by the maker.

<sup>\*\*\*)</sup> De-ionized water with addition of permanganate was distilled four times. Water thus purified will be called simply distilled water in what follows.

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Electrolyzed hydrogen filtered through palladium thimble (called simply hydrogen in what follows) was now introduced over the frozen fuming sulfuric acid by 3 cm Hg pressure, the greaseless tap closed, the content warmed to melt it removing the liquid nitrogen, frozen again by replacing the liquid nitrogen and the greaseless tap opened to evacuate B again. This procedure of melting in hydrogen atmosphere followed by freezing in vacuum was repeated a few times to replace the occluded gas with hydrogen and finally the chain of B and C filled with the same amount of hydrogen over the fuming sulfuric acid was sealed off from the vacuum line at the constriction  $S_1$ . A small portion of sulfuric anhydride was now distilled from B kept at room temperature into A immersed in liquid nitrogen and the latter was sealed off at the constriction  $S_2$  to reject the first portion of distillate. The subsequent portion of sulfuric anhydride was now distilled from B at room temperature to C immersed in liquid nitrogen and B was sealed off at  $S_3$ .

The vessel D was now fused after cleaned as before, as it was wet inside, to C at above  $B_1$  and to the vacuum line at  $J_2$ , evacuated to  $10^{-6}$  mm Hg through a greaseless tap and a trap in liquid nitrogen, filled with hydrogen of 3 cm Hg pressure and then sealed off from the vacuum line at  $S_4$ . An amount of sulfuric anhydride sufficient for the preparation of one batch of aqueous electrolyte for a series of electrolysis experiments was now distilled from C kept at  $50^\circ\text{C}$  into D cooled with tap water by opening the breakable joint  $B_1$  and then the constriction  $S_5$  was sealed off. The remaining portion of sulfuric anhydride in C was reserved for further use with breakable joint  $B_0$  provided for it.

A vessel similar to D was fused to it at above  $B_2$  just as D was previously fused to C and the content of D was distilled into the former just by the similar operations leaving a small quantity of sulfuric anhydride in D. The similar distillation was repeated several times and the final distillate was received in a vessel E as ready for the preparation of the aqueous electrolyte. The vessel E was preliminarily cut off at the broken line across the constriction  $S_6$ , weighted and then replaced by fusing at  $S_6$  in order to determine the final amount of sulfuric anhydride thus obtained by weighing the vessel E sealed off at  $S_6$  with the content.

Water of known deuterium content was prepared as follows from heavy water gifted by Professor T. TITANI of the Tokyo Municipal University or that recovered from used aqueous electrolyte by neutralizing it with anhydrous sodium carbonate "pro analysi" and by distilling the product. The heavy water sample thus obtained was put in vessel F combined with G as shown in Fig. 2, a. The chain of F and G was now fused to the vacuum line at  $J_3$ , the content of F was frozen by liquid nitrogen and the space inside the chain was evacuated to  $10^{-6}$  mm Hg through a greaseless tap and a trap immersed in liquid nitrogen, 3 cm Hg hydrogen introduced into the space and the content of F was melted with the greaseless tap closed. The content was now frozen at  $-40^\circ\text{C}$ , the space evacuated through the greaseless tap and the trap in liquid nitrogen, 3 cm Hg hydrogen introduced and the content was melted again with the greaseless tap closed, which procedure was repeated several times to replace the dissolved gases with hydrogen. Finally, the space was filled with 3 cm Hg hydrogen and the chain of F and G with the content in F was sealed off at  $S_7$ . The content in F was now distilled from  $50^\circ\text{C}$  into G cooled by tap water leaving a small portion in F, which was sealed off at  $S_8$ .

Vessel H was now fused to G at above  $B_4$  and to the vacuum line at  $J_4$ , H and the space communicating with it was evacuated through  $S_9$  to  $10^{-6}$  mm Hg, filled with 3 cm Hg hydrogen and evacuated to wash the wall, filled again with the same amount of hydrogen and the chain

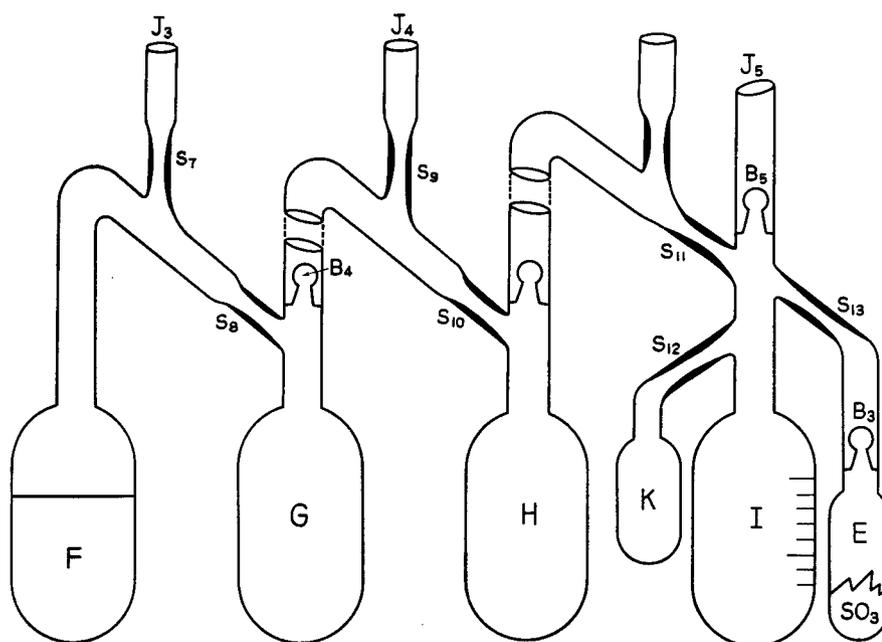


Fig. 2 a. Apparatus for heavy water purification.

$S_7, S_8, \dots, S_{13}$ : constrictions.

$B_5, B_4$ : breakable joints.

$J_3, J_4, J_5$ : junctions to vacuum line.

of G and H was sealed off at  $S_9$ . The breakable joint  $B_4$  was now opened, the content of G was distilled from G kept at *ca.* 50°C into H cooled by tap water leaving a small portion in G, which was sealed off at  $S_{10}$ . Such a distillation was repeated several times as in the case of sulfuric anhydride, receiving the final distillate in a chain of vessels I, E and K fused together as shown in Fig. 2, a; I is graduated to measure the quantity of heavy water inside, E is the container of the final distillate of sulfuric anhydride shown in Fig. 1 and K is an empty vessel of *ca.* 10 cc capacity.  $S_{11}$  was sealed off after heavy water was received in I, a proper portion of heavy water was now decanted into K to leave in I a proper amount of heavy water for the required concentration of the aqueous sulfuric acid as mixed with the sulfuric anhydride in E and then K was sealed off at  $S_{12}$ .

The breakable joint  $B_3$  was now opened, sulfuric anhydride was slowly distilled from E kept at room temperature into I cooled by tap water. A portion of the aqueous electrolyte thus prepared was decanted into E, which was sealed off at  $S_{13}$ , to reserve *ca.* 100 cc aqueous electrolyte in I for one batch of the electrolysis experiment. The reservoir I with the purified aqueous electrolyte was now finished as shown in Fig. 2, b by fusing a piece of glass work shown in the Figure at  $J_5$  with a stay  $S_T$  of hammer L enclosed between  $S_T$  and  $B_5$ ; L is feeted, lest it should choke  $S_T$ , when the whole is set to the electrolytic cell at  $J_6$  invertedly as shown in Fig. 4.

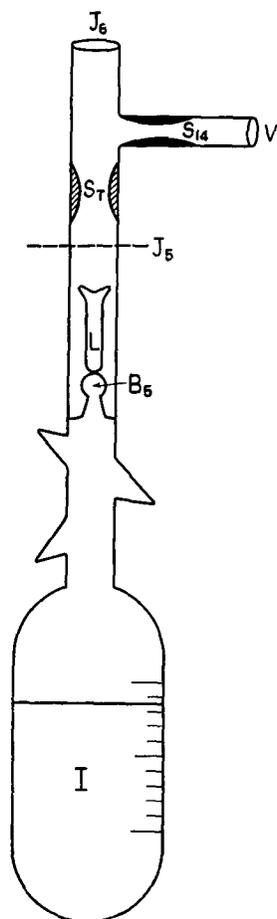


Fig. 2 b.

Heavy water reservoir finished.

S<sub>14</sub>: constriction.

B<sub>5</sub>: breakable joint.

L: hammer.

S<sub>7</sub>: stay for hammer.

V: junction to vacuum line.

J<sub>6</sub>: junction to electrolytic cell.

through it under 2 cm Hg head. The lower tubiform part of the electrolytic cell on the left-hand side of *s* is bent upwards, whereas the right-hand side communicates directly with the upper gaseous space through a vertical tube as shown in Fig. 3 in order to purge bubbles evolved on both sides of *s*, which otherwise accumulate to choke the electrolytic current. The evolution of bubbles is ascribed to the JOULE's heat locally evolved at the filter to liberate

The portion of heavy water separated in K was measured for the deuterium content, whereas that of aqueous electrolyte in E was titrated to determine the concentration of sulfuric acid. The deuterium content of the heavy water was determined by a pycnometer in earlier experiments but later by decomposing heavy water over zinc powder kept at 395°C and by measuring the deuterium content of heavy hydrogen thus obtained by means of the Hitachi massspectrometer of model RMD 3. The deuterium atomic fraction in the heavy hydrogen is identified with that in the heavy water, since the decomposition was practically quantitative, leaving no room for separation to occur. The values of deuterium content as determined both by the methods were found coincident within 0.4% relative difference.

The aqueous electrolyte thus prepared will be called the solution simply in what follows.

## § 2. Electrolytic Cell

Fig. 3 shows the electrolytic cell for the determination of separation factor. P<sub>A</sub> and P<sub>C</sub> are platinum electrodes for preelectrolysis respectively of 1 cm<sup>2</sup> area. C<sub>B</sub> and C<sub>S</sub> are test cathodes, on which the separation factor was determined and A<sub>n</sub> is the anode against the test cathodes. C<sub>B</sub>, C<sub>S</sub> and A<sub>n</sub> are platinum gauze folded into cylindrical form respectively of areas, 59.7, 6.0 and 50 cm<sup>2</sup> as determined from the diameter 0.06 mm of the constituent wire, the specific weight of platinum and their weights. Cathode C<sub>B</sub> or C<sub>S</sub> was used respectively for small or large current density. R<sub>B</sub> and R<sub>S</sub> are the reference electrodes of platinized platinum of 0.2 mm diameter and *ca.* 5 cm length each enclosed in a Luggin capillary, with its lower end held against C<sub>B</sub> or C<sub>S</sub>. The upper parts of the Luggin capillaries were joint and perforated in order to keep hydrogen inside communicating with outside.

The *s* is a glass filter which separates the cathodic compartment from the anodic one; the tightness of *s* was such that it took *ca.* 7 minutes for 10 cc solution to pass through it under 2 cm Hg head. The lower tubiform part of the electrolytic cell on the left-hand side of *s* is bent upwards, whereas the right-hand side communicates directly with the upper gaseous space through a vertical tube as shown in Fig. 3 in order to purge bubbles evolved on both sides of *s*, which otherwise accumulate to choke the electrolytic current. The evolution of bubbles is ascribed to the JOULE's heat locally evolved at the filter to liberate

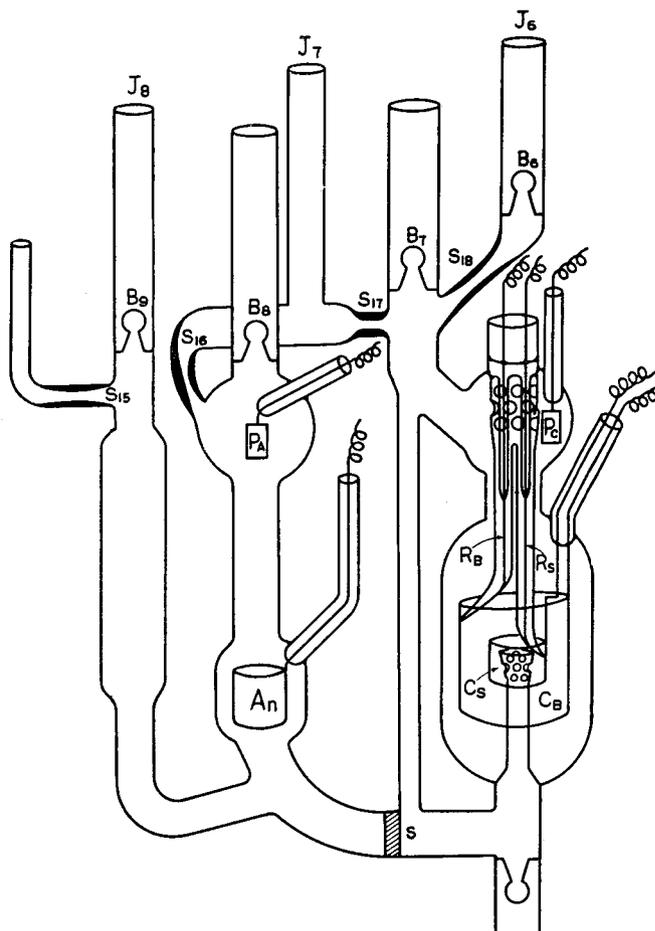


Fig. 3. Electrolytic cell.

- C<sub>S</sub>, C<sub>B</sub>: test cathodes.
- R<sub>S</sub>, R<sub>B</sub>: reference electrode.
- A<sub>n</sub>: anode.
- P<sub>A</sub>, P<sub>C</sub>: electrodes for preelectrolysis.
- S<sub>15</sub>, ..., S<sub>18</sub>: constrictions.
- B<sub>6</sub>, ..., B<sub>9</sub>: breakable joints.
- J<sub>6</sub>, J<sub>7</sub>, J<sub>8</sub>: junctions to vacuum line.
- s: glass filter

dissolved gas. The overall resistance of the electrolytic cell charged with solution amounts to 800  $\Omega$  as determined from the terminal voltage between A<sub>n</sub> and C<sub>B</sub> and the appropriate current.

### § 3. Preliminary Treatment of Electrolytic Cell

The electrolytic cell of Hario glass<sup>\*)</sup> constructed as Fig. 3 was first fused vacant, without

<sup>\*)</sup> cf. footnote<sup>\*)</sup> on p. 46.

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any preliminary treatment, to the vacuum line at  $J_7$ , evacuated down to  $10^{-6}$  mmHg and then left standing overnight, being shut off from vacuum. The cell was taken to be air tight and subjected to the further treatments, if the pressure inside does not thus exceed  $10^{-4}$  mmHg. The volume of one batch of solution for the electrolysis experiment was first determined by putting water into the cell. The reference electrodes  $R_B$  and  $R_S$  were now platinized by putting appropriate solution into the cell and applying current between them alternately. After that the electrolytic cell was rinsed a number of times with distilled water, the reference electrodes were alternately polarized in 1N  $H_2SO_4$  prepared from first class reagent of  $H_2SO_4$  and distilled water by applying current between them and then the electrolytic cell was kept, just as it was, in boiling water with the purpose of removing from the reference electrodes any impurities electrolyzable or soluble in aqueous sulfuric acid.

The electrolytic cell was now filled with 1:1 mixture of conc. sulfuric acid and conc. nitric acid and kept in boiling water for several hours, left standing overnight at room temperature and then heated in boiling water again. The electrolytic cell was now thoroughly rinsed with distilled water, then filled with it and kept in boiling water for several hours renewing the content several times in the meanwhile.

The constriction  $S_{15}$  used for taking in and out of cleaning solution was sealed off, tilting the electrolytic cell to keep water away from  $S_{15}$ . Distilled water inside was now poured out, the cell was fused at  $J_7$  to the vacuum line, as it was wet inside, through a greaseless tap and a trap in liquid nitrogen as in the cleaning of other vessels in §1 and dried by evacuation with precaution not to freeze water inside to crack it. Ascertained that it was evacuated again to  $10^{-6}$  mmHg, the whole electrolytic cell was enclosed in a electric furnace to bake it at  $350^\circ C$  under continuous evacuation for several hours. The electrolytic cell was now filled with hydrogen of 3 cmHg pressure, shut off from vacuum by the greaseless tap, kept at  $350^\circ C$  overnight and then evacuated again. The above procedure of filling with hydrogen of 3 cmHg pressure followed by evacuation was repeated more than three times with the trap kept constantly in liquid nitrogen. Finally the electrolytic cell was filled with hydrogen of 1 cmHg and sealed off from the vacuum line at  $S_{16}$  and  $S_{17}$ .

## § 4. Experimental Procedure

The electrolytic cell thus prepared was now set to compose the apparatus for experiment as shown in Fig. 4. An empty, preliminarily cleaned vessel M was fused to the electrolytic cell at  $J_8$  and to the vacuum line through a greaseless tap N and a trap T immersed in liquid nitrogen as shown in Fig. 4, blowing the fused junctions through T and N. T was kept constantly in liquid nitrogen throughout the series of experiment conducted with one batch of the solution. The M and the joint space was now evacuated, filled with hydrogen of 3 cmHg pressure and then the greaseless tap N was closed.

The I charged with the solution was fused invertedly at  $J_6$ , the hatched space in Fig. 4 evacuated to  $10^{-6}$  mmHg through a trap in liquid nitrogen, sealed off from the vacuum line at  $S_{14}$ , breakable joints  $B_5$  and  $B_6$  were opened to introduce the content of I into the electrolytic cell and I was sealed off at  $S_{18}$ . The thermostat was now filled with water and kept at  $15^\circ C$ . A manostat of 10 l capacity connected to  $C_3$  and  $C_8$  was filled with hydrogen of 12 cmHg pressure, U-tubes  $U_A$  and  $U_C$  were immersed in liquid nitrogen and the space limited by the

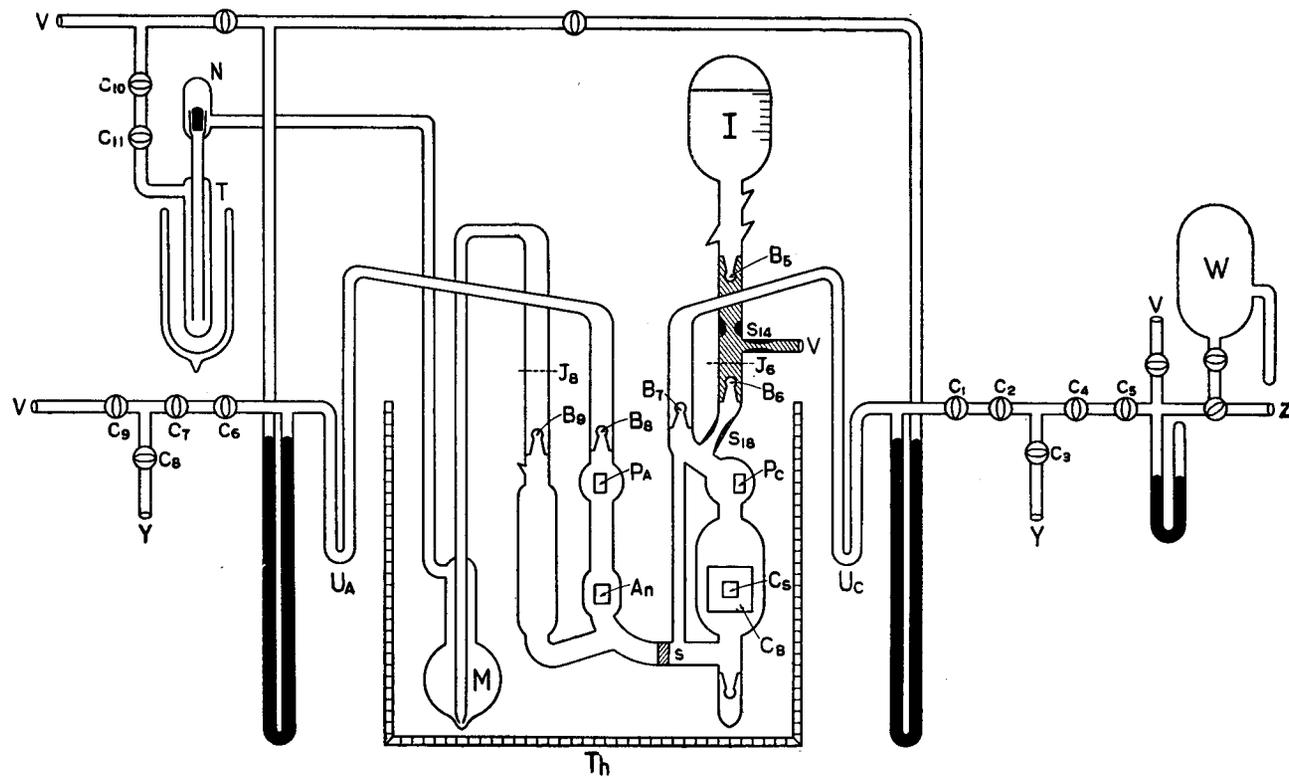


Fig. 4. Electrolytic cell in operation.

- |                                   |  |                                   |
|-----------------------------------|--|-----------------------------------|
| s: glass filter.                  | $B_5, B_6 \dots, B_9$ : breabable joints,    | T: trap.                          |
| $J_6$ : junction to I.            | $S_{14}, S_{18}$ : constrictions.            | Y: junction to manostat.          |
| $J_8$ : junction to M.            | $C_B, C_s$ : test cathodes.                  | Z: junction to diffusion pump and |
| V: junction to vacuum line        | $A_n$ : anode.                               | red hot Pt wire.                  |
| $U_A, U_C$ : U-tubes.             | $P_A, P_C$ : electrodes for preelectrolysis. | $Th$ : thermostat.                |
| $C_1, C_2, \dots, C_{11}$ : taps. | N: greaseless tap.                           |                                   |

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breakable joint B<sub>7</sub>, taps C<sub>3</sub> and C<sub>4</sub>, and the similar space limited by B<sub>8</sub>, C<sub>8</sub> and C<sub>9</sub> were evacuated and filled with hydrogen of 15 cmHg pressure.

Ten mA current was applied between P<sub>A</sub> and P<sub>C</sub> immersed now in the solution and then breakable joints B<sub>7</sub> and B<sub>8</sub> were opened. Taps C<sub>3</sub> and C<sub>8</sub> were opened, having ascertained that the pressure inside them exceeded 12 cmHg and then liquid nitrogen around U<sub>A</sub> and U<sub>C</sub> were removed. The electrolysis between either P<sub>A</sub> and P<sub>C</sub> or A<sub>n</sub> and C was then carried on uninterruptedly throughout the series of experiment with one batch of the solution, where C denotes the cathode consisting either or both of C<sub>s</sub> and C<sub>B</sub>, in order to prevent the diffusion of vapour of tap grease or mercury toward the electrolytic cell. The gas in the manostat was kept at 12 cm Hg by purging it through C<sub>8</sub> and C<sub>9</sub> with C<sub>1</sub> and C<sub>6</sub> closed, whenever the pressure inside exceeded 12 cmHg by a few mmHg.

The preelectrolysis was conducted by applying 30 mA current between P<sub>C</sub> and P<sub>A</sub> for several days. Gas evolved was led into the manostat respectively through C<sub>1</sub>, C<sub>2</sub> and C<sub>3</sub> or C<sub>6</sub>, C<sub>7</sub> and C<sub>8</sub>. The reservoir M was now evacuated, filled with hydrogen of 12 cmHg pressure, B<sub>9</sub> opened, and the level of the solution was lowered to remove it from P<sub>A</sub> and P<sub>C</sub> as follows. The current applied between P<sub>A</sub> and P<sub>C</sub> was increased to 100 mA, the U-tubes U<sub>A</sub> and U<sub>C</sub> in Fig. 4 were immersed again in liquid nitrogen and the hydrogen pressure inside M was gradually reduced by manipulating taps C<sub>10</sub> and C<sub>11</sub> to lower the levels of the solution in the electrolytic cell. Current was now applied between the electrodes A<sub>n</sub> and C as soon as one of the electrodes P<sub>A</sub> and P<sub>C</sub> was detached from the solution. The level was now fixed at desired height by closing the greaseless tap N.

Liquid nitrogen around U<sub>A</sub> and U<sub>C</sub> was now removed, 10 mA/cm<sup>2</sup> current was applied between A<sub>n</sub> and C changing its direction every ten seconds several times to activate them and the reference electrodes R<sub>B</sub> and R<sub>s</sub> were cathodically polarized against A<sub>n</sub> for *ca.* ten seconds in order to saturate the liquid in the LUGGIN capillaries with hydrogen. After these preliminary treatment, C was subjected to a steady cathodic polarization to keep its overvoltage against the reference electrode constant at a required value, leaving taps C<sub>1</sub>, C<sub>2</sub> and C<sub>3</sub> as well as C<sub>6</sub>, C<sub>7</sub> and C<sub>8</sub> open. As the current between A<sub>n</sub> and C had to be interrupted, the solution was raised by increasing hydrogen pressure in M to immerse P<sub>A</sub> and P<sub>C</sub>, and current was applied between them.

The current between A<sub>n</sub> and C was found not to be kept constant at a constant overvoltage but to decay with lapse of time as shown in Fig. 5, which was adjusted to keep the overvoltage constant within 5 mV. Hydrogen was electrolyzed down to point (a) in Fig. 5 two or three times as much as the quantity contained in the cathodic compartment of the electrolytic cell plus the joint space limited by the manometer and tap C<sub>1</sub> at the 12 cm Hg total pressure. Beyond the point (a) the electrolyzed hydrogen was led to the preliminarily evacuated reservoir W of 120 cc capacity up to a few mm Hg pressure through taps C<sub>1</sub>, C<sub>2</sub>, C<sub>4</sub> and C<sub>5</sub> with C<sub>3</sub> closed with a precaution to keep the hydrogen pressure in the cathodic compartment constant within 3 mmHg. C<sub>1</sub> was closed and W and the joint space were evacuated for a few minutes in order to wash the wall of the space. The electrolyzed hydrogen was now collected in W up to 3 cmHg pressure at the point (b) in Fig. 5.

The hydrogen electrolyzed was thus sampled at one constant overvoltage after another successively. As the initial current at a constant overvoltage was found to have decreased to

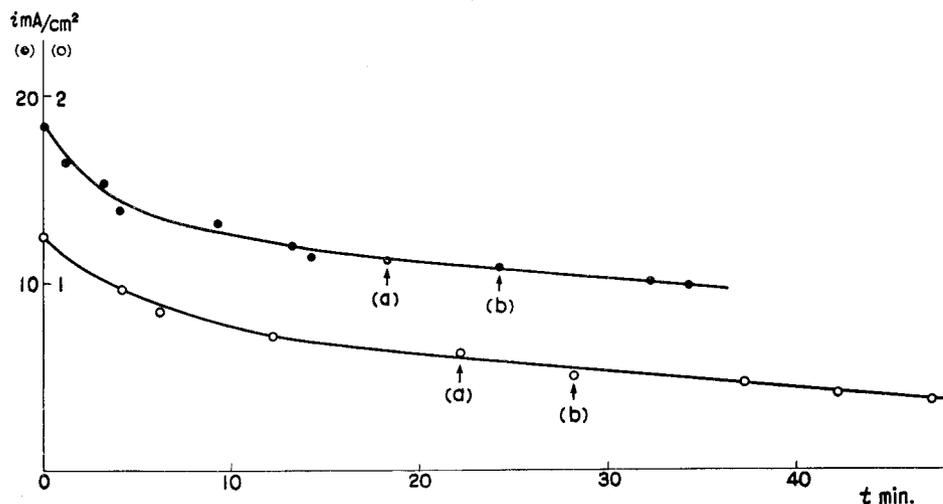


Fig. 5. Dependence on time of current density at constant overvoltage.  
 ● Run No. 8\*)  $\eta=0.15$  V, ○ Run No. 36\*)  $\eta=0.08$  V.

one fifth of that of the first electrolysis at the same overvoltage, the preelectrolysis was resumed by increasing the hydrogen pressure in M to raise the solution to immerse  $P_A$  and  $P_C$ . The preelectrolysis was found almost to recover the initial current, which was conducted for every six to eight consecutive runs of electrolysis each at a constant overvoltage.

The sample collected in W was now circulated over a red hot platinum wire through a trap immersed in liquid nitrogen for 20 to 30 minutes in order to remove oxygen possibly diffused in from the anodic space through the filter s. The electrolyzed hydrogen thus treated was led to another vessel connected with the vacuum line and its deuterium content was determined by means of Hitachi Model RMD 3 massspectrometer.

### § 5. Determination of Separation Factor

Electrolytic separation factor  $S_t$  is defined as

$$S_t = \frac{-\Delta P_t / P_t}{-\Delta D_t / D_t}, \quad (3)$$

where  $-\Delta P_t$  or  $-\Delta D_t$  is the unidirectional rate<sup>\*\*)</sup> respectively of protium  $P$  or deuterium  $D$  transferred by electrolysis from the solution and  $P_t$  or  $D_t$  is the amount respectively of protium or deuterium subject to the electrolysis in the solution. Notation H will be reserved to denote hydrogen without isotopic

\*) The Run No. refers to that in Tabl 2.

\*\*\*) The forward transfer of protium or deuterium by electrolysis is more or less counter-balanced by the backward one; the rate of either is what is called the unidirectional rate here.

discrimination. The directly observed rate of electrolysis either of protium or deuterium is its unidirectional forward rate less the appropriate unidirectional backward one. The unidirectional backward rate is negligible as shown in Appendix 1 at sufficiently large overvoltage.  $S_t$  equals then  $S'$ , *i. e.*

$$S' = \frac{P_g/P_l}{D_g/D_l} = \frac{x_l(1-x_g)}{x_g(1-x_l)}, \quad (4. a)$$

where  $P_g$  or  $D_g$  is the amount of protium or deuterium in the electrolyzed hydrogen gas and  $x_g$  or  $x_l$  is the atomic fraction of deuterium in the gas or the solution respectively.

The general equation for  $S_t$  allowed for the unidirectional backward rate is derived in Appendix 1 in the limiting case of low deuterium content as

$$S_t = \frac{S' - S \exp(-2F\eta/\nu_r RT)}{1 - \exp(-2F\eta/\nu_r RT)}, \quad (4. b)$$

where  $F$  is Faraday,  $\eta$  is the overvoltage<sup>\*)</sup> and  $\nu_r$  is the stoichiometric number of the rate-determining step of the hydrogen electrode reaction responsible for the electrolysis,  $R$  the gas constant and  $T$  the absolute temperature;  $\nu_r$  is unity for the electrochemical and the catalytic mechanism but two for the slow discharge mechanism<sup>\*\*)</sup> as referred to the hydrogen electrode reaction



$S$  is the value  $(D_l P_g / D_g P_l)_{eq}$  of  $(D_l / P_l) / (D_g / P_g)$  at the exchange equilibrium between the solution and hydrogen gas, *i. e.* the partition coefficient of deuterium between them, which is written for the fixed value of  $D_l / P_l$  as

$$S = (P_g / D_g)_{eq} D_l / P_l, \quad (6. a)$$

where suffix *eq* signifies the quantity in equilibrium as in what follows.  $S$  was measured by OKAMOTO<sup>15)</sup> between pure water and hydrogen gas at 0° and 20°C.  $S$ -value at 15°C is interpolated from the result, assuming the linear relation between  $\log S$  and  $1/T$ , as

$$S = 4.13 \pm 0.04, \quad 15^\circ\text{C}, \quad (6. b)$$

which will be identified with that in the present case of the solution.

It is shown on the other hand in Appendix 2 that (4. b) for the limiting case holds practically in the present case of finite  $x_g$  and  $x_l$  within experimental errors.

\*) The overvoltage is defined in the present paper as the negative of the potential of the electrode in question as referred to the reversible hydrogen electrode in the same solution and the same hydrogen atmosphere.

\*\*\*) We have  $\nu_r = 2$  in the case of the slow discharge mechanism, where (2. a) governs the rate, being followed by (2. b).

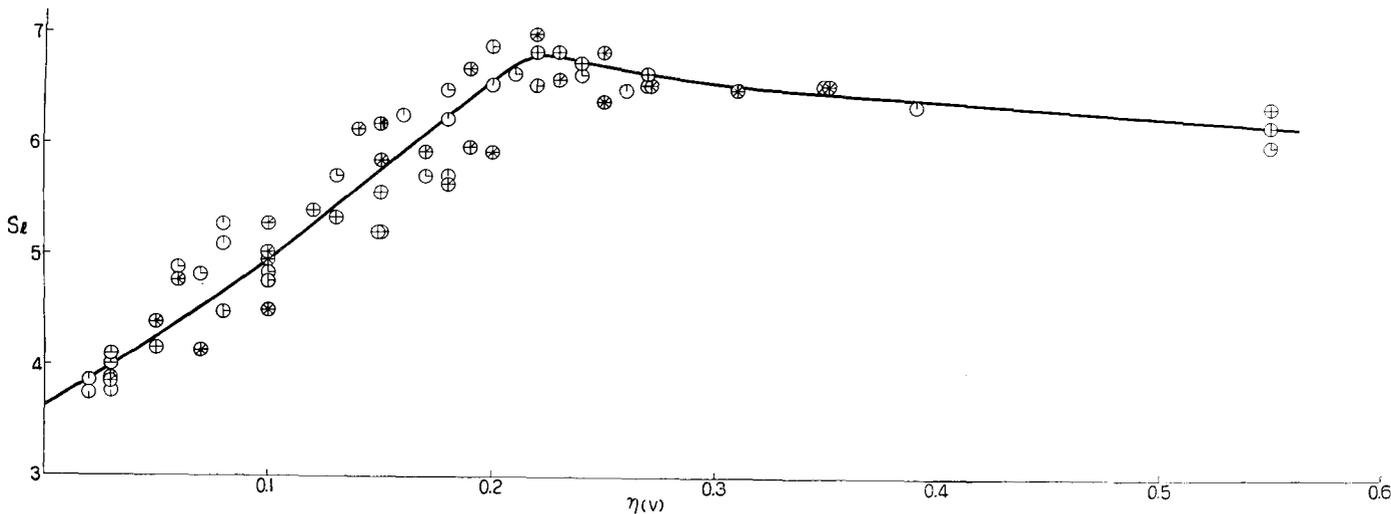


Fig. 6. Electrolytic separation factor  $S_l$  as function of overvoltage  $\eta$ .

○.....⊕ denotes the order of consecutive measurements after each preelectrolysis by number of radii in the circles, e.g., as ○ or ⊕ for the first or the fourth measurement.

TABLE 1. Experimental results of electrolytic separation factor  $S_l$  at 15°C.

Solution : 1.34 N  $H_2SO_4$ ,  $x_l = 0.0849 \pm 0.0003$

Total pressure :  $12.0 \pm 0.3$  cm Hg

No of Runs	Overvoltage $\eta$ volt	$N^{PD}/N^{P_2}$	$N^{D_2}/N^{P_2}$	$100 x_g$	$S'$	$S_l$	No of Runs	Overvoltage $\eta$ volt	$N^{PD}/N^{P_2}$	$N^{D_2}/N^{P_2}$	$100 x_g$	$S'$	$S_l$
6	0.02	0.0473	0.0005	2.30	3.94	3.89	28	0.18	0.0326	0.0002	1.60	5.71	5.71
13		0.0487	0.0005	2.37	3.82	3.74	30		0.0333	0.0001	1.62	5.63	5.63
1	0.03	0.0476	0.0006	2.33	3.89	3.87	41		0.0288	0.0001	1.41	6.49	6.49
2		0.0462	0.0005	2.25	4.03	4.02	62		0.0298	0.0002	1.47	6.22	6.22
9		0.0481	0.0005	2.34	3.87	3.85	17	0.19	0.0311	0.0002	1.53	5.97	5.97
15		0.0455	0.0004	2.21	4.11	4.10	27		0.0278	0.0002	1.37	6.68	6.68
35		0.0492	0.0005	2.39	3.79	3.78	19	0.20	0.0314	0.0002	1.54	5.93	5.93
3	0.05	0.0446	0.0005	2.18	4.16	4.16	40		0.0285	0.0002	1.40	6.53	6.53
18		0.0427	0.0004	2.09	4.35	4.35	56		0.0271	0.0001	1.33	6.88	6.88
32	0.06	0.0382	0.0003	1.87	4.87	4.87	55	0.21	0.0282	0.0001	1.38	6.63	6.63
39		0.0390	0.0003	1.91	4.76	4.77	44		0.22	0.0266	0.0002	1.31	6.99
11	0.07	0.0447	0.0005	2.19	4.14	4.14	38	0.0285		0.0001	1.40	6.53	6.53
63		0.0388	0.0002	1.89	4.82	4.82	59	0.0271		0.0002	1.34	6.83	6.83
31	0.08	0.0368	0.0002	1.79	5.09	5.09	42	0.23	0.0274	0.0001	1.34	6.83	6.83
33		0.0355	0.0002	1.73	5.27	5.27	50		0.0284	0.0001	1.39	6.58	6.58
36		0.0418	0.0003	2.03	4.48	4.48							

No. of Runs	Overvoltage $\eta$ volt	$N^{PD}/N^{P_2}$	$N^{D_2}/N^{P_2}$	$100 x_g$	$S'$	$S_z$	No. of Runs	Overvoltage $\eta$ volt	$N^{PD}/N^{P_2}$	$N^{D_2}/N^{P_2}$	$100 x_g$	$S'$	$S_z$
4	0.10	0.0376	0.0003	1.84	4.95	4.95	47	0.24	0.0281	0.0001	1.38	6.63	6.63
7		0.0391	0.0003	1.91	4.76	4.76	57		0.0278	0.0001	1.36	6.73	6.73
10		0.0371	0.0003	1.82	5.00	5.00	20	0.25	0.0290	0.0002	1.43	6.39	6.39
12		0.0417	0.0004	2.04	4.45	4.45	61		0.0274	0.0001	1.34	6.83	6.83
14		0.0384	0.0003	1.88	4.84	4.84	21	0.26	0.0287	0.0002	1.41	6.49	6.49
26		0.0353	0.0903	1.73	5.27	5.27	46		0.27	0.0287	0.0001	1.40	6.53
29	0.12	0.0344	0.0003	1.69	5.40	5.40	49	0.0282		0.0001	1.38	6.63	6.63
34		0.13	0.0326	0.0002	1.60	5.71	5.71	51		0.0284	0.0002	1.40	6.53
37	0.0350		0.0002	1.71	5.33	5.33	52	0.31	0.0288	0.0001	1.41	6.49	6.49
60	0.14	0.0304	0.0002	1.49	6.13	6.13	22		0.35	0.0287	0.0001	1.40	6.53
5		0.15	0.0317	0.0002	1.56	5.85	5.85	53		0.0285	0.0002	1.40	6.53
8	0.0356		0.0003	1.75	5.21	5.21	58	0.39	0.0292	0.0002	1.44	6.35	6.35
16	0.0334	0.0002	1.64	5.56	5.56	23	0.55		0.0307	0.0003	1.52	6.01	6.01
38	0.0301	0.0002	1.48	6.18	6.18	24		0.0300	0.0002	1.48	6.18	6.18	
54	0.0358	0.0002	1.75	5.21	5.21	25		0.0292	0.0002	1.44	6.35	6.35	
64	0.16	0.0298	0.0001	1.46	6.26	6.26							
43		0.17	0.0313	0.0002	1.54	5.93	5.93						
45	0.0326		0.0002	1.60	5.71	5.71							

### § 6. Results

Table 1 shows the results of the experiment. "No. of Runs" refers to the order of the runs conducted. The third and fourth columns show the ratio of the concentration  $N^{PD}$  of PD to that  $N^{P_2}$  of  $P_2$  and the ratio of the concentration  $N^{D_2}$  of  $D_2$  to  $N^{P_2}$  respectively in the electrolyzed gas as observed directly by the massspectrometer, the third last column gives the atomic fraction of deuterium in the gas calculated from the observed values of  $N^{PD}/N^{P_2}$  and  $N^{D_2}/N^{P_2}$  by the equation

$$x_g = \frac{1 + 2N^{D_2}/N^{PD}}{2(1 + N^{P_2}/N^{PD} + N^{D_2}/N^{PD})} \quad (7)$$

and the second last column shows  $S'$  calculated by (4.a) from  $x_l$  and  $x_g$ . The  $S_l$  in the last column was calculated by (4.b) and (6) from the observed values of  $x_l$ ,  $x_g$  and  $\eta$  for  $\nu_r=1$ . At  $\eta=0.02$  volt,  $S_l$  was found 1.7% or 4.9% lower than  $S'$  according as  $\nu_r=1$  or 2 respectively. The difference between  $S_l$  and  $S'$  is quite small at  $\eta=0.06$  volt and practically vanishes at higher overvoltages, whether  $\nu_r$  be 1 or 2, as seen from (4.b) and (6).

The values of  $S_l$  for  $\nu_r=1$  are now plotted against  $\eta$  as shown in Fig. 6. The  $S_l$  increases as seen in the Figure from 3.6 around the reversible potential steadily up to the maximum value 6.8 around  $\eta=0.23$  volt and then decreases slowly with increase of  $\eta$  down to 6.2 at  $\eta=0.5$  volt. As mentioned in §4, every six to eight consecutive runs of the separation factor measurements, *i.e.* the samplings of electrolyzed hydrogen gas were followed by a preelectrolysis, which almost recovered the current density on C, decaying otherwise at any constant overvoltage along with the continuation of the electrolysis. The separation factors at different overvoltages are indicated in Fig. 6 by circles containing increasing number of radii with the progressing order of runs conducted consecutively between every two successive preelectrolyses, the first and, *e.g.*, the fourth of every consecutive runs being indicated by  $\odot$  and  $\oplus$ . It appears as seen in Fig. 6 that the fluctuation of points has no correlation with the order of the consecutive runs between two successive preelectrolyses.

The relation between the current density and overvoltage was observed as follows after the last preelectrolysis conducted; the solution was lowered as usual for ten minutes and then cathodes  $C_B$  and  $C_S$  combined together was subjected to an overvoltage which was stepwise decreased for 9 min. The result is shown by curve 1 in Fig. 7. After the observation of curve 1, that of curve 2 was initiated immediately, 19 min after the finish of the preelectrolysis. Curves 2, 3 and 4 were similarly observed one after another without break. The time of initiation of each curve after the end of the preelectrolysis is entered

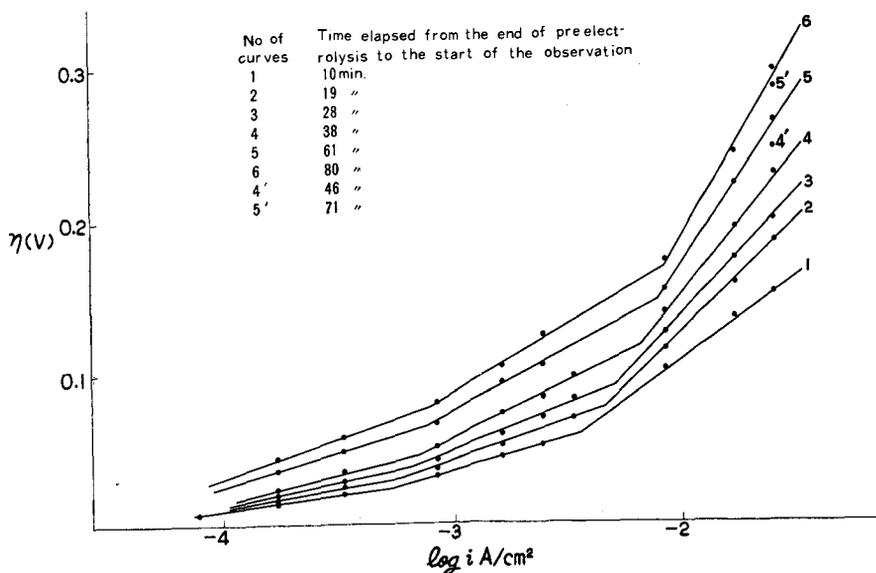


Fig. 7. Tafel line shifting with time.

in the Figure. Point 4' shows the overvoltage observed at the highest current density 25 mA/cm<sup>2</sup>, at which every curve was started, immediately after the completion of curve 4. The observation of point 4' was not followed by those at lower current densities, but the electrolysis at the same current density was continued for 15 min until the observation of curve 5 was started at the same current density. The overvoltage increased in the mean time from that of 4' to that at the start of curve 5. Point 5' shows the overvoltage observed similarly immediately after the observation of curve 5 at the highest current density steadily applied for 9 min until the start of curve 6.

### § 7. Discussion

It is first discussed in this section on the basis of the results in the foregoing section that any transport process, *i.e.* the diffusion of hydrogen or the evaporation of hydrogen into bubbles or the diffusion of hydrogen ion cannot govern the rate.

Fig. 7 shows that the current at any constant overvoltage decays along with the continuation of electrolysis, which is impossible if the rate is governed by any transport process, unless the channels of the transport process is gradually narrowed *e.g.* by deposition of solid particles on the electrode. This is of course very improbable but we will discuss the possibility of the transport

process governing the rate without excluding it.

Let the diffusion of hydrogen molecules be rate-determining. The chemical potential  $\mu^{\text{H}_2}$  of hydrogen  $\text{H}_{2,\eta}$  dammed up by the rate-determining diffusion is expressed as

$$\mu^{\text{H}_2} = 2\mu^{\text{H}^+} + 2\mu^{\epsilon} \quad (8)$$

because of equilibrium of (5) on the electrode as implied in the premise, where  $\mu^{\text{H}^+}$  or  $\mu^{\epsilon}$  is the chemical potential of hydrogen ions or metal electrons in the electrode in question. The  $\mu^{\text{H}_2}$  is given on the other hand in terms of the virtual concentration  $N_{\eta}^{\text{H}_2}$  of hydrogen in gas supposed to be in equilibrium with  $\text{H}_{2,\eta}$  and the value  $\mu_1^{\text{H}_2}$  of  $\mu^{\text{H}_2}$  at unit concentration as

$$\mu^{\text{H}_2} = \mu_1^{\text{H}_2} + RT \ln N_{\eta}^{\text{H}_2} \quad (9)$$

and  $\mu^{\epsilon}$  in terms of overvoltage  $\eta$  and the value  $\mu_{eq}^{\epsilon}$  of  $\mu^{\epsilon}$  at the reversible potential in hydrogen of concentration  $N^{\text{H}_2}$  in gas, as

$$\mu^{\epsilon} = \mu_{eq}^{\epsilon} + F\eta. \quad (10)$$

We have from the above three equations

$$\mu_1^{\text{H}_2} + RT \ln N_{\eta}^{\text{H}_2} = 2\mu^{\text{H}^+} + 2\mu_{eq}^{\epsilon} + 2F\eta$$

Since  $\eta$  should vanish for  $N_{\eta}^{\text{H}_2} = N^{\text{H}_2}$ , we have

$$\mu_1^{\text{H}_2} + RT \ln N^{\text{H}_2} = 2\mu^{\text{H}^+} + 2\mu_{eq}^{\epsilon}.$$

It follows from the above two equations that

$$N_{\eta}^{\text{H}_2} = N^{\text{H}_2} \exp(2F\eta/RT). \quad (11)$$

The current density  $i$  observed is now proportional to  $N_{\eta}^{\text{H}_2} - N^{\text{H}_2}$ , hence  $\ln i$  should increase with increase of  $\eta$  at the rate  $\alpha \equiv (RT/F) \partial \ln i / \partial \eta = 2 \{1 - \exp(-2F\eta/RT)\}^{-1}$  which is equal to or greater than 2 for  $\eta > 0$ . The  $\alpha$  is now less than 2 except at overvoltage below 0.03 volt as deduced from the result of Fig. 7. This value may even be larger than the true value, since the current density at a definite overvoltage steadily decays along with the continuation of the electrolysis, whereas the current was measured at consecutively decreasing overvoltage. It follows that the diffusion of hydrogen molecules could not govern the rate at least for  $\eta > 0.03$  volt.

The diffusion of hydrogen cannot govern the rate, however, even below 0.03 volt overvoltage, since  $S' \leq 4.11$  for  $\eta \leq 0.03$  volt as seen in Table 1, whereas the premise of the diffusion governing the rate leads, as shown below, to the value  $S' \geq 4.87$ .

$\text{H}_{2,\eta}$  is in equilibrium of the reaction

$$P_2 + D_2 = 2PD, \quad (12. a)$$

or

$$\mu^{P_2} + \mu^{D_2} = 2\mu^{PD}, \quad (12. b)$$

for the chemical potentials  $\mu^{P_2}$ ,  $\mu^{D_2}$  and  $\mu^{PD}$  respectively of  $P_2$ ,  $D_2$  and  $PD$  satisfy individually the equations of type of (8), *i. e.*

$$\mu^{P_2} = 2\mu^{P^+} + 2\mu^\varepsilon, \quad \mu^{D_2} = 2\mu^{D^+} + 2\mu^\varepsilon, \quad \mu^{PD} = \mu^{P^+} + \mu^{D^+} + 2\mu^\varepsilon, \quad (13. P_2), (13. D_2), (13. PD)$$

because of the equilibrium of hydrogen with the solution, as implied in the premise, and (13) leads readily to (12. b). It follows from (12. b) that

$$(N_\eta^{PD})^2 / N_\eta^{P_2} N_\eta^{D_2} = K, \quad (14)$$

where  $N_\eta^{PD}$  *etc.* are concentrations of  $PD$  *etc.* under the specified equilibrium at overvoltage  $\eta$  and  $K$  is the equilibrium constant of (12. a).

We have from (13), on the other hand, that the partition coefficient  $(D_l/P_l)(P_g/D_g)_\eta$  of deuterium between the solution and  $H_{2,\eta}$  is given invariantly by  $S$ , *i. e.* the partition coefficient at  $\eta=0$  as shown below, where  $(P_g/D_g)_\eta$  is the value of  $P_g/D_g$  in  $H_{2,\eta}$ . The  $(P_g/D_g)_\eta$  is expressed in terms of  $N_\eta^{PD}$ ,  $N_\eta^{P_2}$  and  $N_\eta^{D_2}$  as

$$\left(\frac{P_g}{D_g}\right)_\eta = \frac{N_\eta^{PD} + 2N_\eta^{P_2}}{N_\eta^{PD} + 2N_\eta^{D_2}}. \quad (15)$$

The  $\mu^{P_2}$  *etc.* are now expressed as  $\mu^{P_2} = \mu^{P_2} + RT \ln N_\eta^{P_2}$ , *etc.* similar to (9), where  $\mu^{P_2}$  *etc.* are the values of  $\mu^{P_2}$  *etc.* at  $N_\eta^{P_2}=1$  *etc.* respectively, hence we have according to (10) and (13)

$$N_\eta^{P_2} = \exp\left(\frac{2\mu^{P^+} + 2\mu^\varepsilon - \mu^{P_2} + 2F\eta}{RT}\right) \text{ etc.} \quad \text{or} \quad N_\eta^{D_2} = N_{eq}^{D_2} \exp(2F\eta/RT) \text{ etc.}$$

where  $N_{eq}^{D_2}$  is the concentration of  $P_2$  in  $H_{2,\eta}$  at  $\eta=0$ . Substituting  $N_\eta^{P_2}$  *etc.* from the above equations into (15), we have

$$\left(\frac{P_g}{D_g}\right)_\eta = \frac{N_{eq}^{PD} + 2N_{eq}^{P_2}}{N_{eq}^{PD} + 2N_{eq}^{D_2}} = \left(\frac{P_g}{D_g}\right)_{eq},$$

hence according to (6. a)

$$\frac{D_l}{P_l} \left(\frac{P_g}{D_g}\right)_\eta = S.$$

The latter equation defines the value of  $(P_g/D_g)_\eta$  by the fixed value of  $D_l/P_l$  and that of  $S$  of (6. b), as

$$\left(\frac{P_g}{D_g}\right)_\eta = S \frac{P_l}{D_l} = S \frac{1-x_l}{x_l} = 44.5 \quad (16)$$

on the base of the value  $x_l=0.0849$ . The  $K$  in (14) is, on the other hand, interpolated from the observation of UREY<sup>21)</sup> assuming that  $\log K$  varies linearly with  $1/T$ , as

$$K = 3.23, \quad 15^\circ\text{C}. \quad (17)$$

The ratios  $N_\eta^{PD}/N_\eta^{P_2}$  and  $N_\eta^{D_2}/N_\eta^{PD}$  are now determined as two roots of the simultaneous equations

*Separation Factor of Deuterium on Platinum Hydrogen Electrode in Aqueous Sulfuric Acid*

(14) and (15) on the base of the data of (16) and (17) irrespective of  $\eta$ , hence identically with  $N_{eq}^{PD}/N_{eq}^{P_2}$  and  $N_{eq}^{D_2}/N_{eq}^{PD}$ , as

$$N_{\eta}^{PD}/N_{\eta}^{P_2} = N_{eq}^{PD}/N_{eq}^{P_2} = 0.0446, \quad N_{\eta}^{D_2}/N_{\eta}^{PD} = N_{eq}^{D_2}/N_{eq}^{PD} = 0.0138. \quad (18. P), (18. D)$$

Eq. (18) shows that  $H_{2,\eta}$  consists almost of  $P_2$  and the same is true with hydrogen around the electrode as seen in Table 1. Eq. (11) is written in consequence with good approximation by replacing  $N_{\eta}^{H_2}$  and  $N^{H_2}$  there by  $N_{\eta}^{P_2}$  and  $N^{P_2}$ , as

$$N_{\eta}^{P_2} = N^{P_2} \exp(2F\eta/RT). \quad (19. a)$$

We have on the other hand from (15) and (16), neglecting  $N_{\eta}^{PD}$  and  $2N_{\eta}^{D_2}$  respectively compared with  $2N_{\eta}^{P_2}$  and  $N_{\eta}^{PD}$ , as

$$2 \frac{N_{\eta}^{P_2}}{N_{\eta}^{PD}} = S \frac{P_l}{D_l}. \quad (19. b)$$

Let now  $D_{PD}$  or  $D_{P_2}$  be the diffusion constant of PD or  $P_2$  molecule respectively. The ratio of the rate of the rate-determining diffusion of  $P_2$  molecules to that of PD molecules is now  $D_{P_2}(N_{\eta}^{P_2} - N^{P_2})/D_{PD}(N_{\eta}^{PD} - N^{PD})$ , which should equal  $N^{P_2}/N^{PD}$ , *i.e.*

$$\frac{N^{P_2}}{N^{PD}} = \frac{D_{P_2}(N_{\eta}^{P_2} - N^{P_2})}{D_{PD}(N_{\eta}^{PD} - N^{PD})}, \quad (19. c)$$

inasmuch as the hydrogen atmosphere consists of the evolved hydrogen itself under the present experimental condition. Eliminating  $N_{\eta}^{PD}/N_{\eta}^{P_2}$  and  $N^{P_2}/N_{\eta}^{P_2}$  from (19), we have

$$\frac{2N^{P_2}}{N^{PD}} \frac{D_l}{P_l} = S \left\{ \frac{D_{P_2}}{D_{PD}} - \left( \frac{D_{P_2}}{D_{PD}} - 1 \right) \exp\left(-\frac{2F\eta}{RT}\right) \right\}.$$

The factor  $2N^{P_2}/N^{PD}$  equals  $P_0/D_0$  by the same approximation as in the case of (19. b), hence we have from the above equation according to (4. a)

$$\frac{S'}{S} = 1 + \left( \frac{D_{P_2}}{D_{PD}} - 1 \right) \left\{ 1 - \exp\left(-\frac{2F\eta}{RT}\right) \right\}.$$

We see  $S' > S$ , since the right-hand side of the above equation is greater than unity, insofar as  $D_{P_2} > D_{PD}$  and  $\eta > 0$  and that  $S'$  increases monotonously from  $S$  to  $SD_{P_2}/D_{PD}$  with increase of  $\eta$ . It may be reasonably assumed that  $D_{P_2}$  and  $D_{PD}$  are proportional to the mean velocity of the thermal motion of  $P_2$ - and PD-molecules, hence to the reciprocals of the square roots masses, *i.e.*  $D_{P_2}/D_{PD} = \sqrt{6}/2 = 1.225$ . We have from the above equation with reference to (6. b), that  $S' = 4.87$  at the lowest overvoltage  $\eta = 0.02$  volt of the observation and  $S' = 5.02$  at  $\eta = 0.04$  volt and 5.07 at  $\eta \rightarrow \infty$ , hence  $S' \geq 4.87$  as stated above.

The evaporation of hydrogen molecules could neither govern the rate of the observed hydrogen electrode reaction, admitted that its rate is similarly proportional to  $N_{\eta}^{H_2} - N^{H_2}$ .

Let now the rate-determining diffusion be alternatively that of hydrogen ion along the descent of the electrostatic potential. Its rate  $r$  per unit area of the electrode surface is  $-DdN^{H^+}/dx - lN^{H^+}dE/dx$ , assuming the one-dimensional diffusion along the coordinate  $x$  normal to the electrode surface, where  $D$  or  $l$  is the diffusion constant or the mobility of hydrogen ion,  $N^{H^+}$

the concentration of hydrogen ion and  $E$  the electrostatic potential; the first term is the rate of pure thermal diffusion and the second one that of electrolytic conduction. Hence we have, with reference to the modified NERNST relation<sup>22)</sup>  $D/RT=l/F$ ,

$$r = -(lN^{\text{H}^+}/F)d\mu^{\text{H}^+}/dx,$$

where

$$\mu^{\text{H}^+} = RT \ln N^{\text{H}^+} + FE + \text{const.}$$

is the electrochemical potential of hydrogen ion.

Let the rate-determining diffusion begin at  $x=0$  and end at the electrode surface, where  $x=X$ . We have from the above expression of  $r$ , which is constant throughout  $x$  at a steady state,

$$\mu_i^{\text{H}^+} - \mu_0^{\text{H}^+} = (rF/l) \int_0^X dx/N^{\text{H}^+}, \quad (20. a)$$

where  $\mu_i^{\text{H}^+}$  is the electrochemical potential of hydrogen ion at  $x=0$ , hence in the bulk of the solution, and  $\mu_0^{\text{H}^+}$  is that at  $x=X$ , *i. e.* at the electrode surface respectively.

The  $\text{H}^+$  at  $x=X$  must be in equilibrium of the reaction  $\text{H}^+ + \varepsilon = 1/2 \cdot \text{H}_2$ , hence

$$\mu_0^{\text{H}^+} + \mu^\varepsilon = 1/2 \cdot \mu^{\text{H}_2}.$$

We have on the other hand in the reversible equilibrium of the whole processes inclusive of the diffusion and the electrode reaction

$$\mu_i^{\text{H}^+} + \mu_{eq}^\varepsilon = 1/2 \cdot \mu^{\text{H}_2},$$

hence from the above two equations

$$\mu_i^{\text{H}^+} - \mu_0^{\text{H}^+} = \mu^\varepsilon - \mu_{eq}^\varepsilon = F\eta$$

according to the definition of  $\eta$ . The rate  $r$  and in consequence the current density  $i$  is given according to (20. a) as

$$i = k\eta/\varphi, \quad (20. b)$$

where  $k$  depends, according to the premise, solely on the geometry of the channels, steadily decreasing along with the continuation of electrolysis and  $\varphi = \int_0^X dx/N^{\text{H}^+}$ . It follows from (20. b), that

$$\left(\frac{\partial \log \eta}{\partial \log k}\right)_i \left(1 - \frac{d \log \varphi}{d \log \eta}\right) + \left(\frac{\partial \log i}{\partial \log k}\right)_\eta = 0,$$

admitting that  $\varphi$  is a function solely of  $\eta$ . The  $\varphi$  is constant and in consequence  $d \log \varphi / d\eta = 0$  in the particular case, where  $N^{\text{H}^+}$  is constant. It is expected in general, that  $N^{\text{H}^+}$  decreases with increase of  $x$  for positive  $\eta$  and thus  $\varphi$  increases with  $\eta$  or  $d \log \varphi / d\eta$  is positive. We have in consequence for a finite decrease of  $k$

$$(\Delta \log \eta)_i > -(\Delta \log i)_\eta \quad \text{for } \Delta \log \eta > 0, \quad (20. c)$$

where  $-(\Delta \log i)_\eta$  and  $(\Delta \log \eta)_i$  are the appropriate decrease of  $\log i$  at constant  $\eta$  and such increase of  $\log \eta$  at constant  $i$  respectively due to a finite decrease of  $k$ .

TABLE 2.  $-(\Delta \log i)_\eta / (\Delta \log \eta)_i$

Pair of curves	$\eta$ Volt	$\log i$ (A/cm <sup>2</sup> )	$-(\Delta \log i)_\eta$	$(\Delta \log \eta)_i$	$-(\Delta \log i)_\eta / (\Delta \log \eta)_i$
1, 2	0.15	-1.665	0.220	0.079	2.8
	0.05	-2.734	0.187	0.064	2.9
2, 3	0.17	-1.732	0.105	0.042	2.5
	0.05	-2.915	0.137	0.061	2.3
	0.03	-3.310	0.185	0.059	3.1
3, 4	0.20	-1.655	0.122	0.045	2.7
	0.08	-2.530	0.200	0.065	3.1
	0.03	-3.495	0.145	0.067	2.2
4, 5	0.20	-1.744	0.143	0.064	2.2
	0.10	-2.419	0.282	0.088	3.2
	0.04	-3.331	0.369	0.152	2.4
5, 6	0.25	-1.656	0.119	0.057	2.1
	0.10	-2.701	0.169	0.060	2.8
	0.04	-3.700	0.162	0.073	2.2

Both the sides of (20.c) were calculated from each pair of contiguous two curves in Fig. 7 as shown in Table 2. The first column of Table 2 shows the pairs of contiguous curves, from which  $-(\Delta \log i)_\eta$  and  $(\Delta \log \eta)_i$  were determined. The second and the third columns specify  $\eta$  and  $\log i$  at a point P on the lower of the pair of curves. The fourth or the fifth column shows the excess  $(\Delta \log i)_\eta$  of  $\log i$  on the higher curve at the  $\eta$ -value of P over that at P or the excess  $(\Delta \log \eta)_i$  of  $\log \eta$  on the higher curve at the  $i$ -value of P over that at P.

The  $-(\Delta \log i)_\eta / (\Delta \log \eta)_i$  amounts to *ca.* 2 to 3 throughout as seen in the last column of the Table, which disproves (20.c) deduced from the premise of the diffusion of hydrogen ion to govern the rate.

It is thus concluded that the rate observed is governed by the genuine chemical reaction on the electrode surface, hence the observed separation factor is specific to the latter.

The experimental results shown in Fig. 6 verifies now the conclusion from the theory on the separation factor<sup>(1)2)</sup>, that it increases from the characteristic value near 3 of the electrochemical mechanism with increase of overvoltage to another characteristic value *ca.* 7 of the catalytic mechanism.

The separation factor decreases, however, as seen in Fig. 6 slowly with further increase of overvoltage. Such decrease of separation factor has been reported by HISANO *et al.*<sup>13)</sup> It is however not conclusive at the moment whether such decrease would verify another theoretical prediction that the electrochemical mechanism is restored at higher overvoltage, since it may result as well, if the catalytic mechanism persists, by local rise of temperature at the electrode surface possibly caused by the heavy current at the high overvoltage, inasmuch as the separation factor of the catalytic mechanism decreases appreciably with rise of temperature<sup>5)7)</sup>. This point may be decided by investigating the dependence on pH of the current density, which is either pronounced or trifling according as the electrochemical or the catalytic mechanism is operative<sup>4)10)16)</sup>.

## Appendix 1

### Derivation of (4. b)

Eq. (4. b) is derived in the limiting case of low deuterium content as follows. The  $S'$  is expressed in general as

$$S' = \frac{\Delta P_t - \Delta P_o}{\Delta D_t - \Delta D_o} \bigg/ \frac{P_t}{D_t},$$

where  $-\Delta P_o$  or  $-\Delta D_o$  is the unidirectional backward rate of protium or deuterium transferred to solution from hydrogen gas. The above equation is written with reference to (3) as

$$S' = S_t \frac{1 - \Delta P_o / \Delta P_t}{1 - \Delta D_o / \Delta D_t}. \quad (21)$$

The forward and the backward unidirectional rates  $\bar{v}$  and  $\bar{v}$  of an elementary reaction are expressed in general as<sup>17)18)</sup>

$$\bar{v} = \kappa kT/h \cdot p^* / p^I, \quad \bar{v} = \kappa kT/h \cdot p^* / p^F, \quad (22. \bar{v}), (22. \bar{v})$$

where  $\kappa$  is the transmission coefficient and  $p^*$ ,  $p^I$  and  $p^F$  are the BOLTZMANN factor of the chemical potentials respectively of the critical complex  $*$ , the initial complex I and the final complex F of the elementary reaction. Consider the forward and the backward rates,  $\bar{v}(P)$  and  $\bar{v}(P)$  of the rate-determining step, which transfers protiums only from the solution to the hydrogen gas or reversely. The ratio of  $\bar{v}(P)$  to  $\bar{v}(P)$  is now according to (22)

$$\bar{v}(P)/\bar{v}(P) = p^{F(P)}/p^{I(P)}, \quad (23. a)$$

where  $p^{I(P)}$  or  $p^{F(P)}$  is the Boltzmann factor of the chemical potential  $\mu^{I(P)}$  or  $\mu^{F(P)}$  of the initial or the final complex of the relevant rate-determining step, hence we have

$$\frac{\bar{v}(P)}{\bar{v}(P)} = \exp\left(\frac{\mu^{I(P)} - \mu^{F(P)}}{RT}\right). \quad (23. b)$$

The affinity  $\mu^{I(P)} - \mu^{F(P)}$  of the rate-determining step is related with the affinity

$$-\Delta F(P) = 2\mu^{P^+} + 2\mu^\varepsilon - \mu^{P_2} \quad (24)$$

of the overall hydrogen electrode reaction of protium



as<sup>19)</sup>

$$\nu_r(\mu^{I(P)} - \mu^{F(P)}) = -\Delta F(P), \quad (26)$$

inasmuch as  $-\Delta F(P)$  is the total sum of the affinities of the constituent steps of (25), whereas the affinities of the constituent steps other than the rate-determining one vanish because of their partial equilibrium. The affinity  $-\Delta F(P)$  vanishes now at the electrode potential, where  $\bar{v}(P)$  and  $\bar{v}(P)$  balance each other, as

$$0 = 2\mu^{P^+} + 2\mu_{eq(P)}^\varepsilon - \mu^{P_2}, \quad (27)$$

where  $\mu_{eq(P)}^\varepsilon$  is the value of  $\mu^\varepsilon$  at the latter electrode potential, which will be called the reversible potential of protium in what follows. We have from (24) and (27)

$$-\Delta F(P) = 2(\mu^\varepsilon - \mu_{eq(P)}^\varepsilon) = 2F\eta_P, \quad (28)$$

where  $\eta_P$  is the negative of the electrode potential as referred to the reversible potential of protium. We have from (23.b), (26) and (28)

$$\bar{v}(P)/\bar{v}(P) = \exp(2F\eta_P/\nu_r RT). \quad (29. a)$$

In the limiting case of low deuterium content  $\bar{v}(P)/\bar{v}(P)$  is identified with

$\Delta P_t/\Delta P_g^{*})$  and  $\eta_P$  with the observed overvoltage  $\eta$ , *i.e.* the negative of the electrode potential as referred to the reference electrode, hence we have

$$\Delta P_t/\Delta P_g = \exp(2F\eta/\nu_e RT). \quad (29. b)$$

The separation factor  $S_g$  in the reverse direction is now defined as

$$S_g = \frac{\Delta P_g}{\Delta D_g} \bigg/ \frac{P_g}{D_g} \quad (30)$$

and reference is made to a theorem verified in a separate paper<sup>20)</sup> in the limiting case, *i.e.*

$$S_t/S_g = S. \quad (31)$$

Eliminating  $S_t$ ,  $S_g$ ,  $\Delta P_g/\Delta P_t$  and  $P_g D_t/P_t D_g$  from (3), (4. a), (29. b), (30) and (31), we have

$$\Delta D_g/\Delta D_t = S/S' \exp(-2F\eta/\nu_e RT). \quad (32)$$

Eq. (4. b) is obtained by substituting  $\Delta P_g/\Delta P_t$  from (29. b) and  $\Delta D_g/\Delta D_t$  from (32) respectively into (21).

It may be noted that (31) holds irrespective of the deuterium content for any reversible hydrogen electrode in a solution and hydrogen gas, which are isotopic exchange equilibrium with each other, according to (3), (6. a) and (30), since then  $\Delta P_g = \Delta P_t$  and  $\Delta D_g = \Delta D_t$ . Such an equilibrium will be called the complete equilibrium in what follows.

## Appendix 2

We have derived (4. b) in Appendix 1 in the limiting case of low deuterium content. Eqs. (29. b) and (31) and the identification of  $\eta_P$  with  $\eta$  are all the relations underlying the derivation, which are exact in the limiting case but not necessarily otherwise. We will investigate these relations in the present case of finite deuterium content with regard to the validity of (4. b).

We first examine the difference  $\eta_P^R$  between  $\eta_P$  and  $\eta$ , *i.e.*<sup>\*\*)</sup>

$$\eta_P^R = \eta_P - \eta, \quad (33)$$

which is the negative of the potential of the reference electrode as referred to

\*) This identification is exact for the slow discharge mechanism irrespective of the magnitude of the deuterium content, since each rate-determining step transfers a single hydrogen nucleus but not for the electrochemical and the catalytic mechanism, where two hydrogen nuclei are transmitted by each act of the rate-determining step, hence  $\bar{v}(P)$  or  $\hat{v}(P)$  does not imply the rate of proton transferred in company with deuterium by one and the same rate-determining step in the respective direction.

\*\*\*) *cf.* p. 67.

the reversible potential of protium. The reference electrode is such one as left without current through it in the same solution and the same hydrogen atmosphere as those around the test cathode C; in the present experiment the deuterium content of the solution is fixed but that of the hydrogen gas depends on the separation factor on C, which evolves hydrogen in the atmosphere. The  $\Delta P_g$  or  $\Delta D_g$  on the reference electrode is not necessarily balanced individually with  $\Delta P_t$  or  $\Delta D_t$ , but in general  $\Delta P_g - \Delta P_t$  and  $\Delta D_t - \Delta D_g$  compensate each other. The  $S_t$  amounts now to *ca.* 3.6 at the potential of reference electrode as extrapolated from the result of Fig. 6. It follows from (6.b), (31)\* and the above value of  $S_t$  that  $S_g = 0.9$ , which indicates in accordance with (30) that the unidirectional rate of transfer  $-\Delta P_g/P_g$  of protium from gas to solution is nearly equal to that  $-\Delta D_g/D_g$  of deuterium or that protium and deuterium behave almost identically with regard to the unidirectional backward rate.

It is hence probable in case of the electrochemical and the catalytic mechanism that the total backward current and  $\bar{v}(P)$  at the potential of reference electrode remain respectively unaffected by the change of isotopic composition of the coexisting hydrogen gas and that  $\bar{v}(P)$  is proportional to the mol fraction  $x(P_2)$  of  $P_2$  in hydrogen gas. These points will be assumed valid in the following estimation. In the case of the slow discharge mechanism it is assumed that  $-\Delta P_g$  is simply proportional to  $1 - x_g$ , whereas  $-\Delta P_t$  remains unchanged irrespective of  $x_g$ . It follows that the complete equilibrium is attained both in the cases at the potential of the reference electrode just by replacing the hydrogen gas with that of the isotopic composition in exchange equilibrium with the solution.

In the case of the electrochemical and the catalytic mechanism we have according to (29. a)

$$\bar{v}(P)^R = \bar{v}(P) \exp(-2F\gamma_P^R/\nu_2 RT) \quad (34. a)$$

and

$$\bar{v}(P)_{eq} = \bar{v}(P), \quad (34. b)$$

where  $\bar{v}(P)^R$  is the rate of  $P_2$  getting into the reversal of the rate-determining step at the potential of reference electrode and  $\bar{v}(P)_{eq}$  is that in the complete equilibrium. Because of the assumed proportionality of  $\bar{v}(P)$  to the mol fraction  $x(P_2)$  of  $P_2$ , we have

$$\gamma_P^R = (RT/2F) \ln x(P_2)_{eq}/x(P_2), \quad (35. a)$$

\* ) Eq. (31) holds exactly either in the complete equilibrium or in the limiting case of low deuterium content and fairly closely for the finite deuterium content in the present experimental condition as shown in Ref. 20.

assigning  $\nu_r=1$  for the electrochemical and the catalytic mechanism, where  $x(P_2)_{eq}$  is the value of  $x(P_2)$  in the complete equilibrium. The  $\eta_p^R$  in the case of the slow discharge mechanism is given similarly for  $\nu_r=2$ , as

$$\eta_p^R = \frac{RT}{F} \ln \frac{1-x_{g,eq}}{1-x_g}, \quad (35. b)$$

where  $x_{g,eq}$  is the atomic fraction  $x_g$  of deuterium in hydrogen in the complete equilibrium.

The  $x(P_2)$  in (35.a) is calculated from the data of  $N^{PD}/N^{P_2}$  and  $N^{D_2}/N^{P_2}$  at different  $\eta$  given in Table 1 by the equation

$$x(P_2) = \{1 + N^{PD}/N^{P_2} + N^{D_2}/N^{P_2}\}^{-1}. \quad (36)$$

The  $x(P_2)_{eq}$  is calculated from the values of  $(N^{PD}/N^{P_2})_{eq}$  and  $(N^{D_2}/N^{PD})_{eq}$  given by (18) according to (36), noting  $(N^{D_2}/N^{P_2})_{eq} = (N^{PD}/N^{P_2})_{eq} (N^{D_2}/N^{PD})_{eq}$ , as  $x(P_2)_{eq} = 0.9565$ . The  $\eta_p^R$  is calculated by (35.a) at different  $\eta$  at 0.2 mV at most in absolute value, which is practically within the errors of  $\eta$ -measurements. The observed  $\eta$  may be in consequence safely identified with  $\eta_p$  according to (33) in this case. The  $x_g$  in (35.b) for the slow discharge mechanism is given in Table 1 and  $x_{g,eq}$  there is calculated from the values of  $(N^{PD}/N^{P_2})_{eq}$  and  $(N^{D_2}/N^{PD})_{eq}$  according to (7). The absolute value of  $\eta_p^R$  calculated from these data at different  $\eta$  is 0.2 mV at most similarly as in the former case. The  $\eta_p$  may thus be practically identified with  $\eta$  in any case of the mechanism.

Eqs. (29.b) and (31) should be, on the other hand, replaced for a finite deuterium content, as shown in a separate paper<sup>20)</sup> in any case of the mechanism, respectively by

$$\Delta P_i/\Delta P_g = f_i \exp(2F\eta/\nu_r RT) \quad (37. a)$$

and

$$S_i/S_g = f_i f_2 f_s S, \quad (37. b)$$

where  $f_i$  differs from unity by less than 1% and  $f_2 f_s$  does by 0.52% at most in the present experimental condition<sup>20)</sup>. We have from (21), (3), (4.a), (30) and (37) by eliminating  $S_g$ ,  $\Delta D_g/\Delta D_i$ ,  $\Delta P_g/\Delta P_i$ ,  $D_i/D_g$  and  $P_i/P_g$  from them similarly as in the case of (4.b),

$$S_i = \frac{S' - f_2 f_s S \exp(-2F\eta/\nu_r RT)}{1 - \exp(-2F\eta/\nu_r RT)/f_i}. \quad (38)$$

The  $S'$  is 3.6 at least in the present experimental condition,  $S$  is 4.13 by (6.b) and  $\exp(-2F\eta/\nu_r RT)$  is 0.22 or 0.50 at most according as  $\nu_r=1$  or  $\nu_r=2$ . It follows that  $S_i$  calculated by (38) deviates from that given by (4.b) within its experimental errors due to those of  $S'$  and  $S$ .

It is thus concluded that (4.b) is applicable in calculating  $S_i$  in the present experimental condition.

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