*The Electrolytic Separation Factor of Hydrogen Isotopes on Metal Electrodes**

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The electrolytic separation factor of hydrogen isotopes (α) usually represents the ratio between the evolution velocities of light hydrogen and heavy hydrogen under the same condition, viz;

$$\alpha=d\frac{(\mathrm{H/D})\ \text{gas}}{(\mathrm{H/D})\ \text{liq.}}$$

So we can get a competent side view for the study of the hydrogen evolution reaction from the measurement of α.

Some investigations were done previously on the problems of how α depends upon the sort of electrode materials, current density and other conditions. According to Horiuti and Okamoto(1), and Walton and Wolfenden(2), α does not vary much with the change of current density, but depends mainly upon the cathode materials. They pointed out that α of many metals were either about 3 or about 6, and that these two groups of α correspond respectively to two different hydrogen electrode mechanisms. Assuming that these two mechanisms exist, Horiuti, Okamoto and Hirota(3) calculated the values of α, and showed the correspondence between the measured value and the theoretical one.

On the other hand, however, these data are lacking in reproducibility. This poor reproducibility may be caused, firstly, by the difficulty in the micro-isotope analysis of hydrogen. Moreover, it is considered that the electrode process of hydrogen evolution reaction is very sensitive to changes of conditions, such as the state of electrode surface or of electrolyte.

Therefore, in order to discuss the mechanisms of hydrogen electrode reaction from the value of α, more extensive works are needed on the point of getting reproducible data. Rome and Hiskey(4) have investigated the separation factor on mercury cathode making use of a mass spectrometer for isotope analysis. Concurrently with Rome and Hiskey, the authors have investigated the separation factor on the various electrodes making use of mass spectrometer, and found some interesting facts about the electrolytic separation factor.

Experimental

Apparatus.—The apparatus used is illustrated in Fig. 1. The capacity of the cell was about 70 cc.

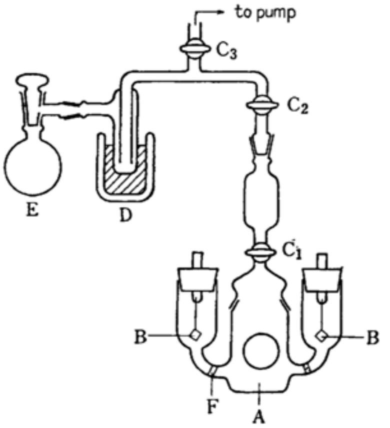

Fig. 1. Schematic diagram of the cell used.
A: Cell
B: Anode
C1, C2, C3: Stop cocks
D: Cold trap
E: Sample bulb
F: Sintered glass disc

As shown in Fig. 1, the cell was divided into three sections separated from each other by a pair of sintered glass discs. Attention was paid to avoid the contamination of electrolyte and electrode surfaces with tap grease.

The cathode part was inserted into the cathode compartment using a glass joint, for which no grease was used. As shown in Fig. 2, the cathode holder was specially devised so that

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* Part of this paper was read at the discussion meeting of the Electrochemical Society of Japan on November 5, 1956.

(1) Horiuti and Okamoto, *Sci. Pap. Inst. Phys. Chem. Res. Tokyo*, **28**, 231 (1936).

(2) Walton and Wolfenden, *Trans. Faraday Soc.*, **34**, 436 (1938).

(3) Horiuti, Okamoto and Hirota, *Sci. Pap. Inst. Phys. Chem. Res. Tokyo*, **29**, 223 (1936).

(4) Rome and Hiskey, *J. Am. Chem. Soc.*, **76**, 5207 (1954).

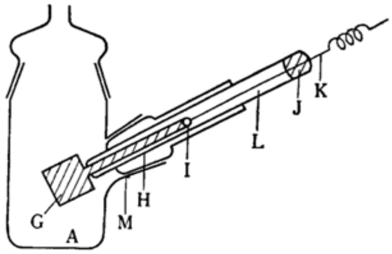

Fig. 2. The cathode and its setting device.

A: Cell
G: Cathode metal
H: Glass tube
I: Solder
J: Paraffin
K: Lead wire
L: Closed air
M: Glass joint

metal parts except cathode might not come into contact with electrolyte.

When mercury was used as the cathode it was put in a little glass vessel which was laid on the bottom of the cell; and a platinum-wire sealed in the glass tube, as in the cases of other cathode materials, was inserted into the mercury without coming into contact with the electrolyte. The surface area of the cathode was in all cases 2 cm^2.

Electrode and Solution.—The separation factor was measured on such cathodes as platinum, gold, silver, nickel, iron, lead, copper, tin and mercury.

The mercury used was purified by electrolysis after distillation. The electrode plates were carefully polished, just before use, with emery paper and washed with distilled water. These electrodes were used repeatedly, being given the same treatment before each experiment. In the cases of iron, nickel, silver and tin, two specimens were used for each metal, but no difference was found between these specimens. The platinum electrode was cleaned, in some cases, by dipping it in concentrated hydrochloric acid at 100°C for an hour, and it was washed with distilled water.

The anodes, two small plates of platinum, had the total surface area of 2 cm^2.

The electrolyte of 0.2 N sulfuric acid solution was prepared from the re-distilled water containing as much deuterium as 0.2 atomic per cent. and guaranteed concentrated sulfuric acid. The solution was then purified by pre-electrolysis for about 15 hours at 0.5 mA/cm^2, and for an hour at 40 mA/cm^2.

Just before the experiment, tank-hydrogen was bubbled into the solution for an hour to saturate the solution with hydrogen and to remove dissolved air.

Procedure.—After setting the electrode to the cell, the hydrogen-saturated solution was poured into the anode compartment. Then it was sucked into the cathode compartment by evacuating this compartment through the cock 1 in Fig. 1.

The cathodic current density was 10 mA/cm^2. It was impossible to prevent entirely the oxygen, evolved by anode reaction, from coming through the glass discs into the cathode compartment, but according to Bockris[5], under such a high current density as in the present experiment, the depolarization effect of oxygen is so small as to be ignored.

The hydrogen gas evolved during the first 15 minutes, being contaminated with the pre-saturated tank-hydrogen, was purged by evacuation. Then, the hydrogen gas evolved during the next 30 minutes was introduced into the evacuated sample bulb, after drying the gas by passing it through a cold trap cooled with a mixture of solid-carbon dioxide and ethanol.

In order to measure the time variation of the value of α, sampling was performed every 30 or 15 minutes as mentioned above. The electrolytic current was never cut off during the run of an experiment. The hydrogen gas gathered in the sample bulb was then analysed on the mass spectrometer, the type of CEC 21—103 A.

For isotope analysis of the solution, the exchange equilibrium method[6] was used. The tank-hydrogen, led to the isotopical equilibrium with the solution at 25°C (equilibrium constant 3.87) by making use of Adams' catalyst for five hours, was analysed similarly on the mass spectrometer.

Results

The data of the electrolytic separation factor are shown in Table I. The values of the separation factor were derived from the following equation;

$$\alpha = 3.87\frac{(\mathrm{D/H})_{\text{evol.}}}{(\mathrm{D/H})_{\text{equil.}}}$$

where the subscripts evol. and equil. designate the hydrogen evolved and the hydrogen equilibrated with the solution, respectively, and the factor 3.87 is the equilibrium constant of the following reaction

TABLE I

THE ELECTROLYTIC SEPARATION FACTOR OF HYDROGEN ISOTOPES ON SEVERAL METALS

0.2 N H_2SO_4 solution containing 0.2 atomic per cent. deuterium.

current density at 10 mA/cm^2

metal	α						average
Fe	6.7	6.9	6.6				6.7
Cu	7.0	6.9	7.1	5.2	5.4	6.4	6.3
Ni	5.7	5.5	6.7	5.4	4.9		5.6
Ag	4.6	4.2	4.6				4.5
Pt	4.4	4.8	4.4	4.3	4.4		4.5
Au	4.1	4.3	5.2	4.1			4.4
Pb	3.7	3.6					3.7
Hg	3.7	3.7	3.8				3.7
Sn	2.6	2.2					2.4

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[5] Bockris, *Chem. Rev.*, **43**, 547 (1948).

[6] Kirshenbaum, "Physical Properties and Analysis of Heavy Water", (McGraw-Hill, 1951) p. 205.

$$(H_2O)_{liq.}+(HD)_{gas} \rightleftarrows (HDO)_{liq.}+(H_2)_{gas}$$

at 25°C.

The values listed above refer to the sample gas evolved during 30 minutes after purging initial gas evolved during first 15 minutes of electrolysis.

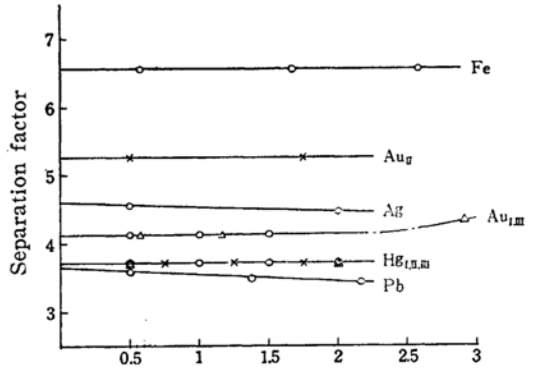

Fig. 3. Time variation of separation factors on several metal cathodes (I). ○, ×, △ designates 1st, 2nd and 3rd run, respectively, on the same metals.

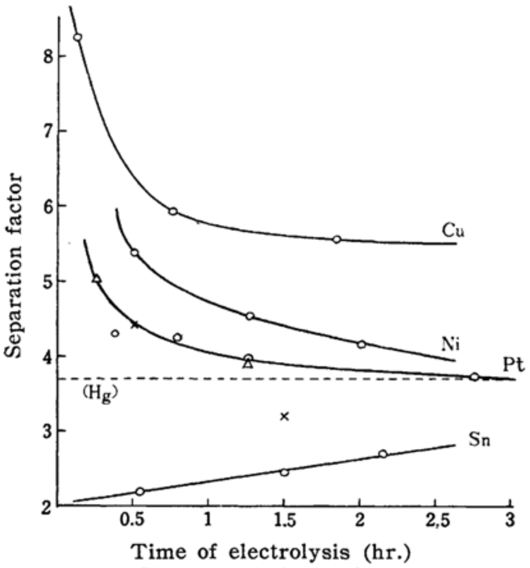

Fig. 4. Time variation of separation factors on several metal cathodes (II). ○, ×, △ designates 1st, 2nd and 3rd run, respectively, on platinum cathode. (Except platinum, typical curves are shown to avoid confusion.)

The time variation of α is shown in Fig. 3 and Fig. 4. In the cases of mercury, iron and gold, values of α were nearly constant in the lapse of time (Fig. 3). As to mercury, values of α obtained in three runs of the experiment coincided within the limit of experimental error, not only in an individual run, but also in all runs of the experiment. On the other hand, for platinum, nickel and copper α decreased with the duration of electrolysis. These decreasing curves of α were lacking in reproducibility, as shown in Fig. 4, but the three runs of the experiments on platinum showed undoubtedly the decrease of α with time. On the contrary, α on tin increased with time (Fig. 4).

Discussion

Time variation of separation factor.—Rome and Hiskey[7] found out that, on mercury cathode, the separation factor decreased markedly when the solution was contaminated with tap grease. Thus, if the cause of the time variation of separation factor in our experiment were imputed to the impurities in the solution, such as dissolved oxygen, tap grease etc., α on mercury, iron and gold must also vary with time. But the fact that not only on mercury but also on iron and gold, the separation factor did not vary with time indicates that the time variation of the separation factor on platinum, nickel etc. was not caused by the effect of impurities.

Apart from this, it may be considered that, since platinum, nickel and copper are all effective catalysts for hydrogen-exchange reaction[8], the secondary exchange reaction of evolved hydrogen gas with the solution may occur at the electrode surface, and as the result of this effect α approaches 3.87, the equilibrium value, with the lapse of time. But in this experiment, evolved hydrogen gas was taken into the sample bulb successively at the same intervals; hence, if decrease of α owes to the secondary exchange reaction, the catalytic activity of electrode surface must increase with time. This increase in catalytic activity with time is also unlikely.

For these reasons, and moreover from the fact that on platinum or nickel the hydrogen over-potential continues to increase for a much longer time than on the other metals[9-11] it may be presumed

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[7] Rome and Hiskey, *J. Am. Chem. Soc.*, **76**, 5209 (1954).

[8] Hirota and Horiuti, *Sci. Pap. Inst. Phys. Chem. Res. Tokyo*, **30**, 151 (1936).

[9] Hickling and Salt, *Trans. Faraday Soc.*, **36**, 1226 (1940).

[10] Bockris and Azzam, ibid., **48**, 153 (1952).

[11] Cousens, Ives and Swaroopa, *J. Chem. Soc.*, **1955**, 3482.

that the time variation of the separation factor is chiefly caused by the hydrogen electrode process itself.

Separation factor and mechanisms of hydrogen evolution reaction.— Horiuti and Okamoto[1)] found out that the separation factors of several metals fell into two groups, viz. ca. 3 and 6, and discussed the fact that these experimental results set forth the mechanisms of the hydrogen evolution reaction, namely the catalytic mechanism for which α was about 6 and the electrochemical mechanism for which α was about 3 at room temperature. Walton and Wolfenden supported this theory, mainly because they found out that the temperature coefficient of α of these two groups showed clearly different tendencies.

However, the measured values of α in our experiment are rather distributed in the range from 2 to 7 at room temperature. For example, α on platinum, silver and gold shows an intermediate value, namely about 4.5. This tendency of distribution can be seen also in the Walton and Wolfenden's results. In their experiments, the separation factors at very low current density (0.03 mA/cm^2) at 15–20°C are as follows[12)]:

Ni : 7.8$_5$, Ag : 6.8, Pt : 5.0,
Hg : 3.5$_5$, Sn : 3.5$_5$.

The fact that the values of α are distributed between 2 and 7 as mentioned above may be explained as follows. The path of hydrogen evolution reaction may not be only one, but probably two or more. If on a cathode metal the evolution of hydrogen took only one reaction path, or at least very predominantly one, separation factors of many metals could be classified according to the mechanisms of hydrogen evolution. This situation was adopted by Horiuti et al. But it is surely possible that on some metals the intermediate state may exist on which the evolution of hydrogen takes several paths in parallel. Supposing this, it is likely that the separation factor has an intermediate value. In addition to this, the value of α will be very sensitive to the condition of the electrode and the solution.

This sensitivity also can be seen, in the case of platinum especially. In our experimental condition α on platinum decreased with the lapse of time, and in addition to this, some preliminary experiments showed that the value of α on the platinum electrode, without any re-treatment after using it once for a run, was ca. 3.6 (the three runs of experiments showed the same results), and that after anodic pre-polarization α had the value higher than before as already reported by Eucken and Bratzler[13)].

Moreover, it must be pointed out that, although, in general, good agreement is seen between the values of α obtained by Walton and Wolfenden and those obtained by Horiuti and Okamoto, in the case of platinum a remarkable discrepancy is found between the two.

These facts may indicate, at least on platinum electrode, that under some conditions the evolution of hydrogen has the possibility of taking several reaction paths in parallel, and that the state of the hydrogen evolution changes with the change of condition of the electrode surface—for example, changes due to pre-treatment of electrode, or to hydrogen saturation of electrode surface with the duration of electrolysis.

Conclusion

According to our experimental data, the values of electrolytic separation factor of hydrogen isotopes on various metals were distributed in the range from 2 to 7. On platinum, nickel and copper, a remarkable time variation of the separation factor was observed. These results do not coincide with the theory of Horiuti and Okamoto, in which two different mechanisms of hydrogen evolution reaction were assumed. The intermediate values of α and the noticeable sensitivity of α on several metals suggest us that it seems rather likely that the hydrogen evolution reaction may take several parallel paths. The time dependence of α may indicate the change of reaction process which follows the change of surface conditions of electrode, probably caused by the electrode process itself.

Considering the above discussion, the measurement of the electrolytic separation factor of hydrogen isotopes will be very useful for the study of hydrogen evolution reaction, though it involves still a complicated aspect. The theory of electrode process at hydrogen evolution is at present yet incomplete, especially in regard to

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12) Walton and Wolfenden, *Trans. Faraday Soc.*, **34**, 444 (1938).

13) Eucken and Bratzler, *Z. phys. Chem.*, **A174**, 273 (1935).

the relation between the reaction and the state of electrode.

From this standpoint, the authors are now studying in more detail the nature of the electrolytic separation factor, especially the relation between the change of over-potential with conditions of electrode and that of the separation factor.

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