Title	DETERMINATION OF THE STOICHIOMETRIC NUMBER OF THE RATE-DETERMINING STEP OF HYDROGEN ELECTRODE REACTION ON Pt AND Rh
Author(s)	MATSUSHIMA, Tatsuo; YOKOYAMA, Takamitsu; ENYO, Michio
Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 17(2), 165-169
Issue Date	1969-08
Doc URL	http://hdl.handle.net/2115/24894
Type	bulletin (article)
File Information	17(2)_P165-169.pdf

(Note)

DETERMINATION OF THE STOICHIOMETRIC NUMBER OF THE RATE-DETERMINING STEP OF HYDROGEN ELECTRODE REACTION ON Pt AND Rh

By

Tatsuo Matsushima[*], Takamitsu Yokoyama[*]
and Michio Enyo[*]
(Received March 20, 1969)

Several investigations have been reported[1,2] on the stoichiometric number, $\nu(r)$, of the rate-determining step of the hydrogen electrode reaction (HER),

$$H_2 = 2H^+ + 2e^-, \qquad (1)$$

where, H^+ is a hydrogen ion associated with Brönsted base, H_2O or OH^-, and e^- is a metal electron. We now intend to determine the value on Rh in alkaline solution and on Pt in both acidic and alkaline solutions. On Pt in alkaline solution, only the value reported was that investigated 30 years ago by Horiuti and Iku-shima.[3] In that work, however, the correction made for the isotope effect of deuterium used as a tracer did not appear to be very reliable because the deuterium separation factor in the HER was assumed to be constant over a wide range of over-potential; in fact, according to later investigations,[4~6] the value near the reversible potential differs from that at highly cathodic overpotential. Therefore, in case the separation factor changes in the potential region concerned, their correction might have introduced a significant error. Further, the equations used for analyzing the data did not take the isotope effect precisely into account.

Recently, a basic equation has been derived[7] with sufficient precaution on the isotope effect, which is applicable for the determination of $\nu(r)$ without introducing those ambiguities. We consider an isotope exchange reaction taking place in a system composed of a catalyst metal (electrode), an electrolytic solution prepared from light water and deuterium gas. For the case that $X_0^g \approx X^g \approx 1$, where X^g is the atomic fraction of deuterium in the hydrogen gas and X_0^g is the value at the outset of the exchange reaction, we have[1] the following equation for ν_{ex}, the experimentally determined value of $\nu(r)$ from an isotope exchange experiment, provided that the deuterium separation factor of HER in the direction of hydrogen ionization is of the order of magnitude of unity,

*) The Research Institute for Catalysis, Hokkaido University, Sapporo, Japan.

T. MATSUSHIMA, T. YOKOYAMA and M. ENYO

$$\nu_{ex} = \frac{\dfrac{2nF}{At}(X_0^g - X^g)}{\dfrac{RT}{2F}\overline{(\partial i/\partial \eta)}_{\eta=0}} \ ,\tag{2}$$

where, t is the reaction time, n is the total number of moles of the hydrogen gas, i is the net current density of HER (positive in the anodic direction), η is the "overpotential" defined as potential of the test electrode as referred to the isotopic mixed potential[7] of the same electrode in the same environment and A is surface area of the test electrode. The quantity $\overline{(\partial i/\partial \eta)}_{\eta=0}$ designates the mean value of $(\partial i/\partial \eta)_{\eta=0}$ over the reaction time, the latter (reaction admittance) being determined throughout the exchange reaction by measuring η and i near the isotopic mixed potential.

Experimental apparatus and procedures were analogous to those reported previously.[2] In parallel with observations of the exchange rate and the reaction admittance, the isotopic composition of the gaseous hydrogen after the exchange experiment was determined and the data were also employed in discussing the reaction mechanism.

Results and Discussion

A. Blank Tests

Blank tests were conducted with regard to both the exchange reaction between deuterium and water and the isotopic equilibration between light hydrogen P_2 and deuterium D_2, $P_2 + D_2 = 2PD$, in 0.5N NaOH using a similar reaction vessel but with no catalyst metal. In experiments started with either pure deuterium ($X_0^g = 0.992$) or with a mixture gas of P_2 and D_2 (free from PD, $X_0^g = 0.251$), no shift was observed of the X^g value from X_0^g or of the isotopic composition after 120 hours of shaking at 12°C. Absence of contribution from a sulfuric acid solution to both the exchange and equilibration reaction was already reported.[2]

B. Diffusion of Hydrogen Molecule

Under the present experimental condition, $i.e.$, total hydrogen pressure of $ca.$ 20 cm Hg, shaking of the reaction vessel at 400 times per minute over 2 cm amplitude and the reaction temperature of 12°C, the diffusion rate of hydrogen molecule towards the electrode should amount to at least 2×10^{-3} A cm^{-2}.[2] This is more than one order of magnitude greater than i_0 (see Table 2) observed on Pt in aqueous sulfuric acid, which was the most active among three cases studied in this work. It follows that the diffusion of hydrogen molecule cannot be rate-determining in all cases of the exchange reaction.

C. Isotopic Mixed Potential during the Exchange Reaction

The isotopic mixed potential should be established on each electrode because

of no diffusion control as mentioned above. The observed potential values, E_{obs}, of the test electrode during the exchange reaction measured as referred to the reference electrode (Rh or Pt) are listed in Table 1.

TABLE 1. Potential of the test electrode, E_{obs}, and the isotopic
mixed potential, E_m, during the exchange reaction.
(Potentials in mV; $X^g \approx 1$, 12°C)

Solution	1.0 N H_2SO_4 *aq.*	0.5 N NaOH *aq.*	
Electrode metal	Pt	Pt	Rh
E_{obs}	0.0 (r. Pt)*)	$-1.5 \sim -2.1$ (r. Rh)	$+3.2 \sim +3.9$ (r. Pt)
E_m	$+1.5$	$+2.4 \sim +1.8$	$+5.5 \sim +6.2$

*) (r. Pt) *etc.* means that E_{obs} was measured against a Pt reference electrode
etc. under the same condition.

On Pt in the acidic solution, a good agreement was observed between the potentials of the test and the reference electrodes. This indicates establishment of the isotopic mixed potential on both electrodes. The value of the isotopic mixed potential, E_m (as referred to the reversible hydrogen electrode in the light hydrogen system under otherwise the same condition), therefore, would be equal to the reported value, $+1.5$ mV.[8] In the alkaline solution, E_{obs} was measured against a Rh reference electrode. Since the E_m-value of Rh electrode was $+3.9$ mV[11] in alkaline solution under the condition $X^g \approx 1$, at 25°C, we add this value to E_{obs} and obtain the E_m-value of the Pt test electrode to be $+2.4 \sim +1.8$ mV. This agrees with the literature value, $+2.3$ mV.[8]

In the case of the Rh electrode in alkaline solution, E_{obs} was rather close to its literature E_m-value, $+3.9$ mV. Adding to this the E_m-value for Pt in alkaline solution, $+2.3$ mV, we obtain E_m for the Rh electrode of $+6.2 \sim +5.5$ mV, which is in poor agreement with the above figure, $+3.9$ mV. It is likely that the Pt reference electrode in this experiment did not assume its E_m. The isotopic mixed potentials were thus not entirely reproducible in alkaline solution.

D. ν_{ex}, Isotopic Composition of Hydrogen Gas and Mechanism.

Results on ν_{ex} are summarized in Table 2. In all the systems studied, the ν_{ex}-value was found to be unity within the experimental error of about 10%. Also listed in this table is the isotopic composition of hydrogen gas given in terms of ρ and ρ', respectively defined as,

$$\rho \equiv \frac{X_{PD}}{X_{PD, eq.}} \quad \text{and} \quad \rho' \equiv \frac{X_{PD} - X_{PD, 0}}{X_{PD, eq.}},$$

where, X_{PD} is mole fraction of PD in the hydrogen gas, $X_{PD, 0}$ is that at $t = 0$ and

TABLE 2. Results of exchange reaction between deuterium and light water. P_{H_2}, total hydrogen pressure at working temperature (12°C); $i = 2nF \ (X_0^G - X^G)/At$; for other symbols, see text.

Run 1. Pt, 1.0N H_2SO_4, $A = 20.0 \ cm^2$, $X_0^G = 0.998$

No	P_{H_2} (cmHg)	n (m mole)	t (hr : min)	X^G	i_0 (A cm^{-2})	$\overline{(\partial i/\partial \eta)}_{\eta=0}$ (mho cm^{-2})	ν_{ex}	ρ	ρ'
1	16.8	2.72	6 : 00	0.903	1.15×10^{-4}	9.25×10^{-3}	1.01	0.13	0.10
2	18.2	2.94	7 : 10	0.914	0.924	7.50	1.00	0.12	0.10
4	16.9	2.70	6 : 20	0.903	1.09	8.35	1.06	0.16	0.13
5	17.1	2.71	4 : 00	0.915	1.50	12.3	0.99	0.19	0.18
6	17.1	2.71	4 : 20	0.902	1.61	11.7	1.12	0.19	0.16
	Average						1.04		0.13

Run 2. Pt, 0.5N NaOH, $A = 162 \ cm^2$, $X_0^G = 0.992$

1	17.5	3.06	3 : 35	0.949	1.26×10^{-5}	9.64×10^{-4}	1.06	0.30	0.13
2	14.1	2.46	3 : 30	0.949	1.00	8.15	1.00	0.28	0.11
3	23.2	4.02	3 : 44	0.966	0.994	7.72	1.04	0.34	0.09
4	26.7	4.59	5 : 00	0.968	0.716	5.31	1.09	0.38	0.12
	Average						1.05		0.11

Run 3. Rh, 0.5N NaOH, $A = 14.5 \ cm^2$, $X_0^G = 0.992$

1	26.4	3.96	18 : 00	0.961	2.57×10^{-5}	1.82×10^{-3}	1.15	0.80	0.59
2	25.7	3.81	27 : 00	0.967	1.34	1.00	1.09	0.86	0.61
3	23.1	3.30	47 : 35	0.968	0.636	0.541	0.96	0.84	0.44
	Average						1.07		0.55

$X_{PD,eq}$. is the value when the same gas was equilibrated with respect to the reaction, $P_2 + D_2 = 2PD$. The quantity ρ is the degree of equilibration with respect to this reaction, while ρ' is the value corrected for PD existed at the beginning of the exchange reaction.

On Pt electrode in alkaline solution, Notoya and Matsuda[9] have observed no dependence of overvoltage upon pH of the solution and hence concluded that the recombination step of hydrogen adatoms determines the overall rate of HER (the catalytic mechanism). The present result, $\nu_{ex} = 1$, supports their conclusion. Also, the value $\rho' \approx 0$ is consistent with this mechanism, because in this mechanism deuterium concentration in the hydrogen adatoms must be extremely low owing

to a rapid exchange between these and light water and hence the chance of formation of PD should be far smaller than that of P_2. The coincidence of the ν_{ex}-value reported by HORIUTI and IKUSHIMA[3] with the present result, in spite of insufficient precaution for the isotope effect in the former work, would probably mean that changes with overpotential of the deuterium separation factor was insignificant in the potential region covered in their work.

On Pt electrode in acidic solution, the $\nu(r)$-value was reported by SCHULDINER[10] to be unity, but his method is subjected to criticism as discussed previously.[2] The value was thus first determined in this work on a solid base. The present results, $\nu_{ex}=1$ and $\rho'\approx0$, are simliar to those obtained above in alkaline solution, but we need more information before reaching at a mechanistic conclusion.

On Rh electrode in alkaline solution, the results, $\nu_{ex}=1$ and $\rho'\approx0.6$ were similar to those observed in aqueous sulfuric acid.[2] The catalytic mechanism was concluded[2] in the latter system, but the value $\rho'\approx0.6$ is not consistent with this mechanism; we probably need to assume concurrent occurrence of a side reaction which gives rise to the isotopic equilibration reaction. Not much is known at present on details of the assumed side reaction.

References

1) M. ENYO, T. YOKOYAMA and M. HOSHI, This Journal, **13**, 222 (1965).
2) T. MATSUSHIMA and M. ENYO, *ibid.*, **17**, 13 (1969).
3) J. HORIUTI and M. IKUSHIMA, Proc. Imp. Acad., Tokyo, **15**, 39 (1939).
4) H. BUTTLAR, W. VIELSTICH and H. BARTH, Z. Electrochem., **67**, 650 (1963).
5) T. YOKOYAMA and M. ENYO, This Journal, **15**, 207 (1967).
6) T. YOKOYAMA, *ibid.* **15**, 84 (1967).
7) M. ENYO and T. YOKOYAMA, Electrochim. Acta, **12**, 1631 (1967), This Journal, **13**, 71 (1965).
8) M. ENYO and T. YOKOYAMA, Electrochim. Acta, **12**, 1641 (1967·)
9) R. NOTOYA and A. MATSUDA, This Journal, **14**, 192 (1966).
10) S. SCHULDINER, J. Electrochem. Soc., **106**, 891 (1959).
11) T. YOKOYAMA, unpublished data.