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DEPENDENCE UPON pH OF THE RATE OF DEUTERIUM EXCHANGE BETWEEN HYDROGEN AND WATER ON NICKEL CATALYST

By

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Abstract

Experimental studies were carried out on the dependence upon solution pH (7~13) of the rate of deuterium exchange between hydrogen and water on nickel catalyst, both in presence and absence of supporting electrolyte. The exchange rate was found to be independent of the solution pH throughout the systems chosen: KOH, KOH+KCl, $NaOH+NaClO_4$ and $KOH+K_2SO_4$. The facts strongly support the theory that the hydrogen electrode reaction on nickel in alkaline solution obeys the catalytic mechanism.

Introduction

The mechanism of the hydrogen electrode reaction (HER) in alkaline solution,

$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^- , \qquad (1)$$

on nickel has been studied repeatedly in the past, and two opposite views have been expressed, *viz.* assuming that the overall reaction consists of two consecutive steps,

$$2\left[H_2O + e^- \longrightarrow H(a) + OH^-\right], \qquad (2.a)$$

and

$$2H(a) \longrightarrow H_2 , \qquad (2.b)$$

some authors have proposed that the first step is rate-determining[1] (in the slow-discharge mechanism), others hold that the second step (in the catalytic mechanism) is rate-determining.

There has been a certain amount of experimental evidence for the slow-discharge mechanism to be operative on nickel: (i) the overpotential at constant polarization current depends upon pH of the solution[1], (ii) a linear Tafel relation with 0.12 v slope[1,2] has been frequently observed, and (iii) the value

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of the stoichiometric number, ν, of the rate-determining step has been reported to be two[2]. The first piece of evidence has, however, been criticized[3] with regard to possible inclusion in the reported results of the ohmic overpotential which could depend on the solution pH. The second observation has been interpreted as well on the basis of the catalytic mechanism by taking into account the mutual interaction among the hydrogen intermediates on the electrode surface[4]. The value of ν has later been found to be unity[5] in disagreement with the third observation. It seems, therefore, that the view of the slow-discharge mechanism to be operative on nickel is ill-founded. Conversely, these facts clearly support the catalytic mechanism and, further, later experimental findings such as the observation of a cathodic saturation current density[6] at ca. 10^2 Amp/cm^2 and of an anodic one[7] at ca. 10^{-5} Amp/cm^2 (the limiting current due to diffusion of molecular hydrogen in solution should be far greater than this figure) and the results of a detailed analysis of the transient behavior of the electrode[8] are all in good harmony with this mechanism.

Studies on the isotopic composition of the gaseous hydrogen obtained by the exchange reaction between pure deuterium and light water catalyzed by nickel catalyst, however, did not support this mechanism[9]. Thus, the composition of the hydrogen obtained was not very far from that in equilibrium with respect to the reaction,

$$P_2 + D_2 = 2PD\,, \qquad (3)$$

(P and D are, respectively, protium and deuterium atoms), whereas, if the catalytic mechanism is operative, production of P_2 only is expected by the exchange reaction, *i.e.*, the gas composition should be out of equilibrium, since the adsorbed hydrogen atoms must consist entirely of protium when the discharge step is rapid, provided only that there exists light water in large excess over the amount of deuterium gas (as is nearly always the case) and that hence the probability of PD formation is quite negligible as compared with that of P_2. This observed fact can, on the contrary, be easily explained on the basis of the slow-discharge mechanism because step (2. b) is rapid in this case. However, because of the abundant evidence for the catalytic mechanism mentioned above, this result has been interpreted in the previous paper, not to be due to the operation of the slow-discharge mechanism but to that of a side reaction within the catalytic mechanism which causes isotopic equilibration independently. It was desirable to obtain further evidence to confirm the catalytic mechanism. Therefore, the dependence upon solution pH of the rate of the deuterium exchange which takes place through the path of the HER is studied in this work.

Theoretical

The rate of the HER is expected to be dependent upon the solution pH when the slow-discharge mechanism is operative. According to FRUMKIN[10], the relation between the forward unidirectional current density i_f and the hydrogen overpotential η is given (in alkaline solutions) as

$$\eta = (RT/\alpha F) \ln i_f - (RT/F) \ln [OH^-] - \phi_1 + \text{const.}, \qquad (4)$$

where ϕ_1 is the potential difference across the diffuse part of the double layer in Stern's model, α is the cathodic transfer coefficient (experimentally, close to 0.5), $[OH^-]$ the OH^- concentration in the bulk of the solution, and the other notations have their usual significance. In a solution with univalent ions, ϕ_1 is expressed[10] approximately as a function of only the total concentration of the univalent cations, $[Me^+]$, as

$$\phi_1 = (RT/F) \ln [Me^+] + \text{const.} \qquad (5)$$

In the absence of supporting electrolyte in an alkaline solution, where $[Me^+] = [OH^-]$, it follows from Eqs. (4) and (5) that

$$\eta = (RT/\alpha F) \ln i_f - (2RT/F) \ln [OH^-] + \text{const.} \qquad (6)$$

and hence the dependence of i_0 (value of i_f at $\eta = 0$, *i.e.*, the exchange current density) upon pH is obtained as

$$\partial \log i_0 / \partial \mathrm{pH} = 2\alpha\,, \qquad (7.\,a)$$

but in the presence of an excess amount of supporting electrolyte, where $[Me^+]$ is approximately constant, the dependence becomes

$$\partial \log i_0 / \partial \mathrm{pH} = \alpha\,. \qquad (7.\,b)$$

Contrary to this, no pH-dependence of i_0 is expected in the case where the catalytic mechanism is operative. Consequently, studies on the pH-dependence should clearly distinguish between the two mechanisms. The deuterium exchange reaction is utilized here because of the already demonstrated fact[5] that the exchange rate definitely represents i_0, and because of the advantage to be free from disturbance by the ohmic overpotential.

Experimental

Apparatus

The reaction vessel (150～190 cc), equipped with 5～8 breakable joints, was similar to that reported elsewhere[9,11]. Nickel wire used as the catalyst (99.99 %, Johnson-Matthey & Co., London, apparent surface area: 485 cm^2)

was wound into a cylinder. Water was obtained by fourfold distillation under flow of nitrogen (evaporated from liquid nitrogen), of which the first two distillations were conducted from alkaline $KMnO_4$ solution.

The solutions were prepared using special grade $NaClO_4$, KCl or K_2SO_4, degassed repeatedly by vacuum operations[11] and stored in a closed solution container equipped with a breakable joint. The solution pH was later shifted by adding under vacuum a known amount of NaOH or KOH solution prepared and degassed separately. Deuterium (>99.5 %, Showa Denko, Kawasaki, Japan) was purified by filtering through a heated palladium thimble.

Procedure

The reaction vessel containing the nickel catalyst was cleaned with hot NaOH solution ($\sim 2N$) for at least one day, followed by repeated rinsing with hot distilled water. It was then fused, together with the solution container, to a vacuum line with liquid nitrogen traps in between. After drying the vessel by evacuation, it was heated in an electric furnace regulated at 350°C. The nickel was oxidized by admitting air twice into the vessel via the traps, each time for 15 min. Oxide formed was then reduced with hydrogen ($\sim$ 10 cm Hg) at the same temperature for two hours, while renewing the hydrogen four times. After evacuation down to 10^{-5} mm Hg, the whole system was sealed off from the vacuum line at a constriction, the solution was introduced into the reaction vessel by opening the breakable joint above the solution container, and then the emptied container was removed. The reaction vessel was again fused to a vacuum line by means of a breakable joint, deuterium gas ($\sim$20 cm Hg) was introduced by breaking this joint, and the vessel was finally sealed off. It was then kept at a fixed temperature (10$\sim$50°C) by means of a super-thermostat and the exchange reaction conducted by shaking it at 240/min with 4 cm amplitude. After a recorded time, the solution was frozen by dipping the vessel in liquid nitrogen, and the hydrogen gas was sampled through a breakable joint. The reaction was repeated similarly under various conditions.

Analysis

The sample gases were analyzed by a gas-chromatograph[5]. The solution pH was determined by a glass-electrode pH-meter.

Results and Discussion

The rate of the exchange reaction, given here in terms of the exchange current density, i_0', was calculated by the equation,

TABLE 1. Results of deuterium exchange reaction under various conditions of pH, temperature and supporting electrolyte on nickel

Apparent surface area of catalyst: 485 cm^2, $D_0 \simeq 1.00$, P_{H_2}: total hydrogen pressure in cm Hg at the reaction temperature, n: total number of moles of hydrogen gas, i_0': exchange current density, i_0: exchange current density normalized at $P_{H_2}=20$ cm Hg by Eq. (9), and ρ: degree of isotopic equilibration as defined in Eq. (11).

Run 1. KOH without supporting electrolyte

No.	pH	Temp. (°C)	P_{H_2} (cm Hg)	t (10^4 sec)	n (m mol)	D	i_0' (μA/cm^2)	i_0 (μA/cm^2)	ρ
1	7.0	29.7	17.2	4.32	1.09	0.55	6.00	6.47	0.87
2	7.0	10.5	18.3	8.58	1.23	0.60	2.88	3.01	0.99
3	9.7	11.6	16.0	8.60	1.05	0.61	2.41	2.69	0.89
4	9.7	29.7	21.0	4.10	1.28	0.56	7.17	6.99	0.90
5	12.6	29.7	18.3	4.02	1.11	0.53	6.89	7.19	0.93
6	12.6	11.1	17.9	8.64	1.14	0.65	2.28	2.41	0.98
7	12.6	50.2	22.3	2.15	1.25	0.35	24.8	23.5	0.94
8	12.6	39.3	20.5	2.87	1.17	0.49	11.6	11.5	0.91

Run 2. KOH with supporting electrolyte (0.5 N KCl)

1	7.0	30.0	17.0	4.80	1.02	0.77	2.23	2.42	0.91
2	7.0	13.5	20.0	8.94	1.27	0.83	1.07	1.07	0.80
3	9.6	14.4	17.3	3.51	1.07	0.96	0.48	0.52	0.82
4	9.6	30.0	20.9	4.26	1.22	0.82	2.17	2.12	0.85
5	12.7	30.0	21.1	7.90	1.22	0.65	2.61	2.54	0.89

Run 3. NaOH with supporting electrolyte (0.5 N $NaClO_4$)

1	8.5	11.3	20.2	4.26	1.68	0.42	13.6	13.6	1.0
2	8.5	31.9	24.4	5.56	1.89	0.16	24.8	22.5	1.0
3	10.2	11.1	19.8	8.73	1.62	0.41	6.53	6.57	0.97
4	10.2	31.6	21.6	5.20	1.63	0.15	23.5	22.6	1.0
5	12.8	11.3	21.1	8.71	1.70	0.43	6.60	6.43	0.91
6	12.8	31.3	22.8	5.12	1.71	0.23	19.8	18.6	0.92
7	12.8	52.3	23.6	2.08	1.64	0.23	46.5	42.8	0.90

Run 4. KOH with supporting electrolyte (0.5 N K_2SO_4)

1	7.0	30.5	23.2	4.37	1.66	0.31	17.7	16.4	0.94
2	7.0	12.5	21.0	8.79	1.58	0.46	5.57	5.44	0.94
3	10.2	12.2	21.4	8.74	1.59	0.49	5.19	5.02	0.93
4	10.2	30.9	22.0	4.63	1.52	0.31	15.2	14.5	0.92

$$i_0' = (2nF/At)\ln(D_0/D), \tag{8}$$

where D_0 is the initial value of the atom fraction of deuterium in the gas phase (almost equal to unity), D the value at time t, A the apparent surface area of the catalyst and n the total number of moles of the gaseous hydrogen. This value of i_0' was then converted to i_0 which is normalized at $P_{H_2}=20$ cm Hg, in order to take into consideration the effect of minor differences in the total hydrogen pressure between individual runs upon the exchange current density, using the relation

$$i_0 = i_0'(20/P_{H_2})^{\beta}, \tag{9}$$

where β was taken to be 0.5 from the previous work[9]. Results obtained under various conditions are listed in Table 1.

Dependence of i_0 and heat of activation upon pH of the solution

As shown in Fig. 1, i_0 was found to be independent of the pH of the solution over the entire range studied (7~13), irrespective of the presence or absence of supporting electrolyte*). The heat of activation defined by

$$\Delta H^* = -R\left(d\ln i_0/d(1/T)\right), \tag{10}$$

was found to be *ca.* 8~10 kcal/mole, also independent of pH and composition of the solution. Typical Arrhenius plots are shown in Fig. 2.

The observed facts contradict those expected above (Eqs. (7)) for the slow-discharge mechanism, but are in harmony with the theory of the catalytic mechanism. Hence, the latter mechanism can be safely concluded to be operative on nickel in alkaline solution on the basis of the present additional evidence, besides the one cited above.

The degree of equilibration of the gaseous hydrogen isotopes is defined in terms of the quantity,

$$\rho = P_{PD}/P_{PD,eq}, \tag{11}$$

where P_{PD} is the partial pressure of PD in the sample gas and $P_{PD,eq}$ that when the same gas is brought to equilibrium with respect to the reaction of Eq. (3). The value of ρ previously reported[9], 0.7~0.9, has been approximately reproduced in this work as 0.8~1.0 (the last column of Table 1). This value is not congruent with the catalytic mechanism, where ρ should be zero, as mentioned in the Introduction.

*) In the perchlorate system, a slight dissolution of nickel during the exchange reaction has been detected. Hence, the results obtained there would be less reliable than those in the other systems.

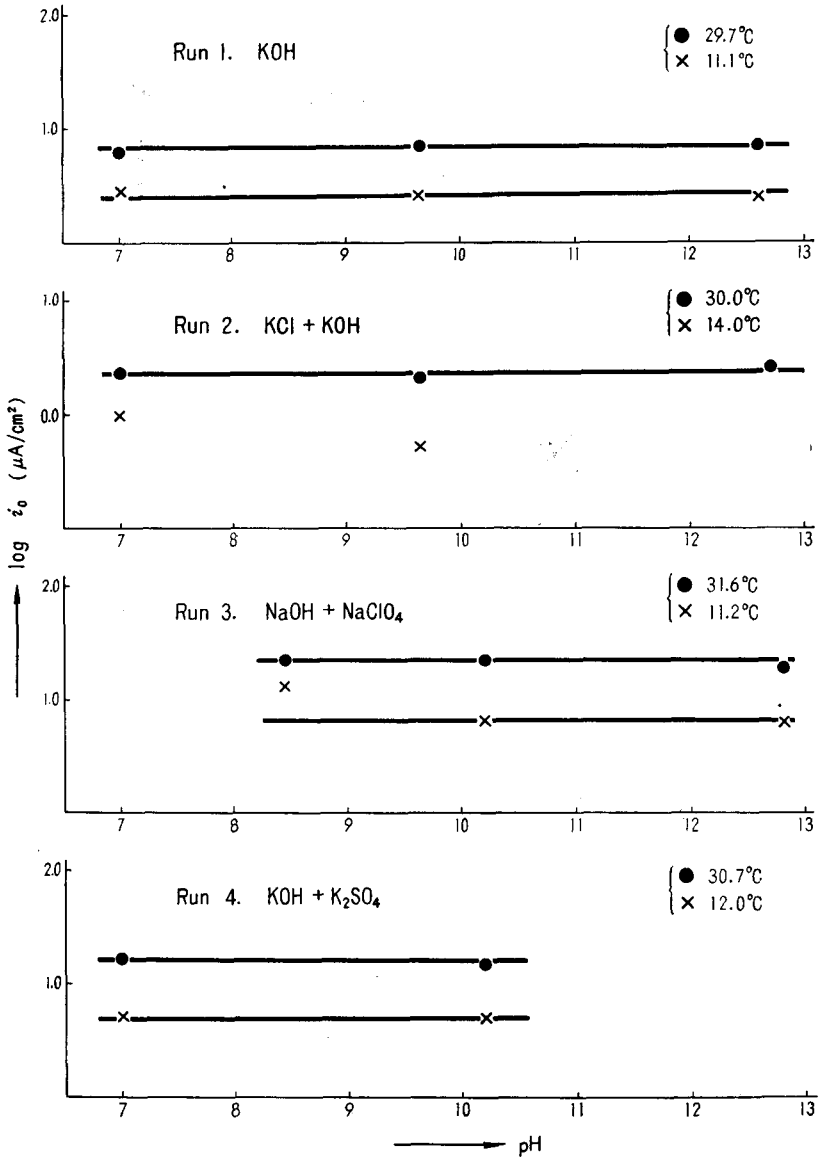

Fig. 1.

Dependence upon pH of the deuterium exchange rate between hydrogen and water on nickel

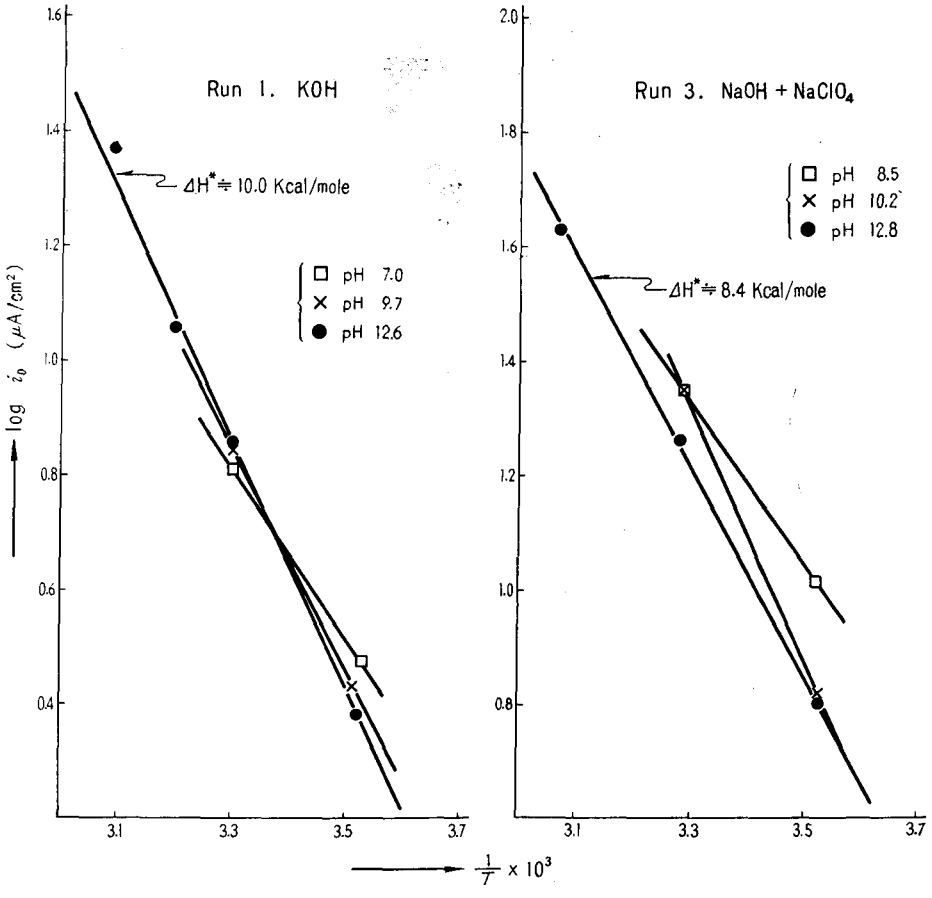

Fig. 2.

Typical Arrhenius plots of the deuterium exchange rate on nickel

It seems inevitable from the above conclusion on the mechanism to take into consideration the possibility of a side reaction which produces PD from P_2 and D_2 concurrently with the exchange reaction. It has been proposed[9] before that the side reaction would be taking place by means of the Rideal-Eley mechanism,

$$D_2 + P(a) \longrightarrow PD + D(a), \qquad (21)$$

which contributes, not only to the production of PD, but also to the exchange reaction by its combination with the rapid discharge step. However, it has

been demonstrated in later work[5] that, at least for moderately smooth nickel catalysts, there exists no side reaction which contributes to the exchange reaction. It is hence likely that the side reaction is taking place by mean of the Langmuir-Hinshelwood mechanism,

$$P_2(a)+D_2(a) \longrightarrow 2PD\,, \tag{13}$$

which, due to lack of a step which splits the hydrogen molecule into atoms, does not contribute to the exchange reaction. This problem will be dealt with separately later.

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