$x-y$ relationship assumed hyperbolic for first point, linear thereafter; calculation started from the carbon disulfide end ($x = 1$).

0.828	645.1	0.721	...	...	0.712
.919[a]	614.1	.799	5.550	.054	.788[b]
1.000	512.3	...	...	...	...

[a] $x' = 0.081 = 1-x$. [b] y' calc. $= 0.212 = 1-y$.

TABLE IV

CHLOROFORM AND ACETONE

Data from J. v. Zawidzki.[1d] $t = 35.17°$.

$x-y$ relationship assumed linear; calculations started from C. B. M. ($x = 0.625$); x and y are mole fractions of chloroform.

x	P	y (obs.)	S_0	b	y (calc.)
0	344.4	0	...	...	...
0.1	323.3	0.050	...	...	0.048
.2	303.5	.115	...	...	.108
.3	283.8	.201	...	...	.194
.4	267.3	.312	...	...	.298
.5	254.0	.445	...	...	.437
.625	248.0	.625	...	...	...
.750	255.6	.800	...	...	.812
.850	269.0	.900	...	...	.910
.950	284.5	.971	...	...	.976
1.000	293.1	1.000	...	...	...

$x-y$ relationship assumed hyperbolic; calculations started from acetone end ($x = 0$).

0.1	323.3	0.050	−0.626	−0.280	0.058

$x-y$ relationship assumed hyperbolic; calculations started from chloroform end ($x = 1$).

0.95[a]	284.5	0.971	−0.583	−1.750	0.978[b]

[a] $x' = 0.05$. [b] y' calc. $= 0.022$.

Summary

A stepwise approximate integration is presented for the Duhem-Margules equation, which makes possible the calculation of the vapor-liquid composition curve from the isothermal total-pressure curve alone.

CAMBRIDGE 39, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, No. 432]

THE VELOCITY OF THE HYDROGEN ELECTRODE REACTION ON PLATINUM CATALYSTS

BY LOUIS P. HAMMETT

RECEIVED AUGUST 18, 1923

The reversible reaction $H_2 \rightleftarrows 2H + 2e$ may be considered a step in many if not all reactions in which hydrogen is produced or in which it reacts. Conditions affecting the velocity of the electrochemical reaction should therefore be of fundamental importance in the study of the numerous chemical reactions of which it forms a part. In particular the close parallelism between the catalysis of the electrode reaction and the catalysis of the combination of hydrogen and oxygen may be mentioned.[1] The measurement of polarization curves on hydrogen electrodes gives the velocity of the reaction as proportional to the current, and the "driving force" of the reaction as a function of the potential. A comparison of these easily measurable quantities for catalysts of different properties gives a quantitative measure of the catalytic activity of the electrode. It is the purpose of the present work to study the relationship between these three variables.

The apparatus was of conventional type, except for the provision of very powerful agitation of the solution in the neighborhood of the electrode under observation. This working electrode was a circular platinum foil 1.2 sq. cm. in area, and coated on the back and edges with flux glass. It was placed horizontally with a glass propeller rotated at high velocity at a distance of 2 to 3 cm. above it. The stirrer worked through a water seal in the stopper of the cell and could be driven at speeds as high as 2000 r. p. m. The polarizing potential was measured against a hydrogen electrode in the same solution but in another cell, the connecting siphon being drawn down to a fine capillary which just touched the working electrode. Current which entered the solution through the working electrode left through a large platinized gauze electrode above the stirrer, whose large area prevented fluctuations due to variations in its polarization, and excluded evolution of anodic oxygen. The sealed stirrer and an exit trap prevented ingress of atmospheric oxygen, and a continuous stream of hydrogen maintained a state of saturation. All measurements were made in a thermostat at 25.00°.

For the purposes of the present work electrolytic tank hydrogen was satisfactory after it had been passed through a heated tube containing palladized asbestos. The water was redistilled in the continuous still in this Laboratory. Hydrochloric acid was not specially purified; potassium hydroxide was purified through the amalgam, and gave no precipitate with barium chloride.

The potential difference was measured with a potentiometer, and the current by using the same potentiometer to determine the potential drop across a resistance or 100 or 1000 ohms. The precision of the electrical measurements was considerably better than the reproducibility of the results.

It was shown by Beans and Hammett[1] that a bare platinum electrode can be given a high catalytic activity for the hydrogen-hydrogen ion reaction by anodic oxidation, and that the catalytic activity thus obtained undergoes a slow decay under the action of hydrogen;[2] also that a bright

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[1] Hammett, *Dissertation,* Columbia University, **1923**.

[2] In the work of Beans and Hammett this decay was noted with carefully purified hydrogen prepared by the electrolysis of sodium hydroxide solution as well as with the tank hydrogen used here.

platinum electrodeposit has an activity almost as great as that of platinum black on an electrode of the same area. It is thus possible to obtain an electrode of any desired activity without even the change in area occasioned by platinizing, and to plot a family of curves representing the current-potential relationship for a wide series of catalytic activities.

In Table I are given the results of typical measurements which cover the range of catalytic activities studied. The data for 0.1 *N* acid are plotted in Fig. 1. The following considerations have been kept in mind in these measurements.

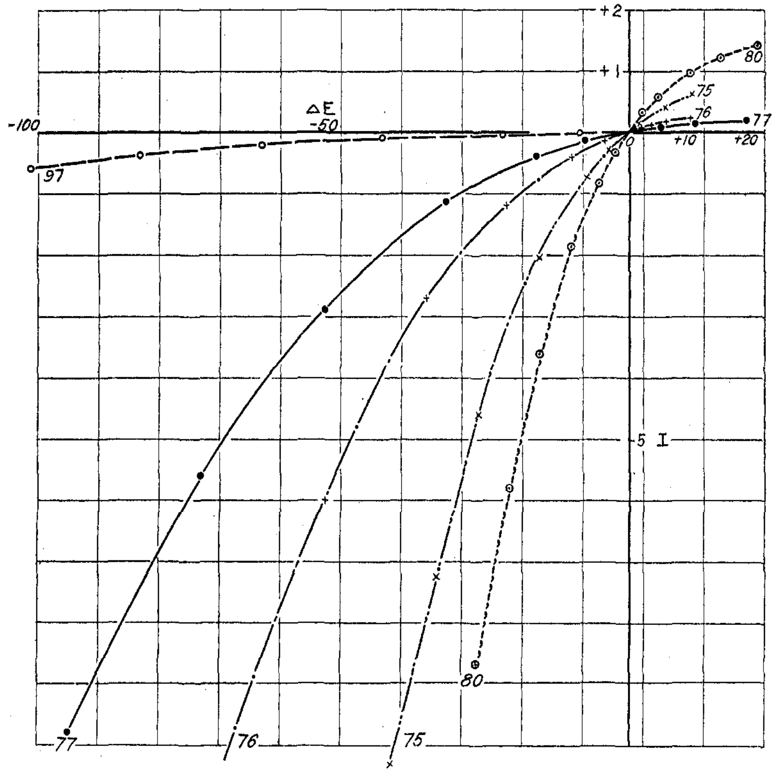

Fig. 1

In an investigation on the velocity of the chemical reaction effects due to concentration polarization must be minimized. Experiment showed that at stirrer speeds between 500 and 2000 r. p. m. the polarization was independent of the stirring. This, of course, proves only that concentration polarization had been reduced to the lowest point possible with the type of stirring used. Furthermore hydrogen evolution at the electrode has at no time been observed. It should be pointed out that the tendency for supersaturation or unsaturation with respect to hydrogen is merely local, since hydrogen is used up at one electrode as fast as it is formed at the other.

The current on first applying a potential may in general be expected to be different from the steady state. Such a steady state was, however, established in most cases more rapidly than the first measurement could be made. With the least active electrodes, such as in Expts. 93 and 97 the time required at the higher potentials was as much as 5 or 10 minutes. Due attention was always paid to this factor.

An electrode in a hydrogen solution suffers a slow decrease in activity. The mere fact of polarization may produce permanent change in activity, such as the increase produced by fairly large anodic polarization. After increasing the polarization to the maximum value in a given experiment one or two measurements were made with decreasing potential. The satisfactory agreement of these values, which are marked with an asterisk (*) in the tables, is evidence of the constancy of the catalytic activity during an experiment.

Measurements on the anodic side were in general less certain and reproducible than on the cathodic side. At 15 to 20 mv. the values began to oscillate rapidly, and at somewhat higher potentials a permanent increase in activity resulted. The qualitative course of these curves at higher potentials, showing first a steady current and then characteristic passivity phenomena, is known from work of other investigators.[3] This of course sets a limit on the range over which anodic polarizations could be satisfactorily measured. In the cathodic side measurements were not pushed far above 10 milliamperes in order to keep concentration polarization low.

The consideration of the results is greatly simplified by the fact that within certain limits the members of the family of curves differ only in the scale of ordinates. That is, the data satisfy the equation

$$E = f\left(\frac{I}{K}\right) \tag{1}$$

where K, independent of potential and current, is a function of the state of the electrode and of the solution, and measures quantitatively the catalytic activity of the electrode. This relationship was found by Haber and Russ[4] to hold for the family of curves obtained for the reduction of nitro compounds when the concentration was varied. Table II shows the ratios of the currents for constant potential but different activities, obtained from large scale plots of the curves. The agreement in the values of R is perhaps all that could be hoped for, in view of the unstable nature of a platinum catalyst, except for the values at high currents, and those with catalysts of

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[3] Sackur, *Z. physik. Chem.*, **54**, 647 (1906). Weigert, *ibid.*, **60**, 546 (1907). Bennewitz, *ibid.*, **72**, 217 (1910).

[4] Haber and Russ, *ibid.*, **47**, 257 (1904).

low activity, for instance in Expts. 93 and 97. In the former case the deviations are probably due to concentration polarization, in the latter they seem rather to be caused by increased experimental difficulty due to slow attainment of the steady state than to be due to any fundamental effect on the velocity of the reaction.

In view of the very low activity for the combination of hydrogen and oxygen of a platinum catalyst in an alkaline solution,[5] it was of interest to compare the activities of catalysts for the hydrogen-electrode reaction in acid and alkaline solutions. Immediately after a powerful anodic oxidation, a bare electrode gave in 0.1 *N* potassium hydroxide solution currents which indicated an activity about one-tenth of that observed with the least active electrode measured in 0.1 *N* hydrochloric acid solution (Expt. 97) and 0.0003 the activity of a freshly oxidized bare electrode in the acid solution. A polarization curve was run on a plated electrode in alkali, the cell was emptied and cleaned and refilled with acid. The ratio of the currents in acid and alkali solutions was 21, but the marked dependence of the polarization in the acid solution upon the rate of stirring showed that concentration polarization was considerable with an electrode of such high activity and the true ratio of the activities is probably higher. Moreover, the necessary exposure of the electrode to the atmosphere might be counted upon to affect its activity. There can, however, be little doubt that the velocity of the hydrogen-hydrogen ion reaction on platinum is much greater in acid than in alkaline solutions, showing again close parallelism with the hydrogen-oxygen reaction.

To determine further the effect of hydrogen-ion activity upon the reaction velocity, measurements of polarization were made upon hydrochloric acid solutions and the cell was then opened sufficiently to allow the introduction of a portion of strong acid without interruption of the hydrogen stream. Preliminary experiments showed that it was possible to open the cell in this fashion without affecting the polarization very greatly. The concentration of the acid was determined by titration after the measurements were made. In this way the following results were obtained.

Expt. 1

Concn.	0.1 *N*		1.135 *N*	
E...............	−10.8	−22.0	−10.3	−20.5
I................	0.071	0.211	0.085	0.325

Expt. 2

Concn.	0.01 *N*			0.1144 *N*		
E.......	−10.7	−21.1	+17.6	−9.9	−20.8	+18.8
I........	0.066	0.157	0.046	0.089	0.240	0.054

From these figures the current ratios were determined graphically, and found to be for Expt. 1, 1.56 and 1.71, for 10 and 20 mv., respectively.

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[5] Hofmann, *Ber.*, **49**, 2369 (1916); **53B**, 298 (1920); **55B**, 573, 1265 (1922).

The average reduced by proportion to a concentration ratio of 10 is 1.43. From Expt. 2 the ratios are 1.58, 1.56 and 1.14. Neglecting the figure 1.14 derived from the anodic polarization as less reliable, the average corrected to a concentration ratio of 10 is 1.25. While hydrogen-ion activity affects the velocity of the reaction, it enters only as a very low power.

The equilibrium on a hydrogen electrode is given by the following equation[6]

$$2\mu_{H^+} - \mu_{H_2} - 2FE = 0 \qquad (2)$$

where μ refers to the potential (or partial molal free energy) of the substance given by the subscript. The velocity functions for the two opposing reactions must be compatible with this when the velocities are equal. The expressions most in conformity with the velocity function for an ordinary chemical reaction, and with the generally exponential course of polarization curves are given by Equation 3 or 4, either of which reduces to Equation 2 when the velocities of the opposed reactions are set equal. It will be seen that reaction velocity is here made proportional to activity rather than to concentration, a procedure now common.

$$v_1 = k_1' e^{\frac{2\mu_{H^+} - 2FE}{RT}} \qquad (3a) \qquad\qquad v_1 = k_1' e^{\frac{2\mu_{H^+} - FE}{RT}} \qquad (4a)$$

$$v_2 = k_2' e^{\frac{\mu_{H_2}}{RT}} \qquad (3b) \qquad\qquad v_2 = k_2' e^{\frac{\mu_{H_2} + FE}{RT}} \qquad (4b)$$

Equation 3 shows the velocity of oxidation of hydrogen independent of potential, and indicates positive polarization curves rising to a maximum, which is in accord with the experimental data. The current is proportional to the difference in velocity of the opposed reactions and is given by

$$I = k_2 e^{\frac{\mu_{H_2}}{RT}} - k_1 e^{\frac{2\mu_{H^+} - 2FE}{RT}}$$

By application of the criterion that $I = 0$ for an unpolarized electrode

$$k_2 e^{\frac{\mu_{H_2}}{RT}} = k_1 e^{\frac{2\mu_{H^+}}{RT}} e^{-\frac{2FE_0}{RT}}$$

$$\text{and} \quad I = k_2 e^{\frac{\mu_{H_2}}{RT}} \left(1 - e^{-\frac{2F\Delta E}{RT}}\right)$$

$$\text{or} \quad I = k_2 a_{H_2} \left(1 - e^{-\frac{2F\Delta E}{RT}}\right) \qquad (5)$$

where E_0 is the equilibrium potential, ΔE the polarizing potential, and a_{H_2} the activity of dissolved hydrogen.

The values of $k_2 a_{H_2}$ are given in Table I. The constancy is good within 15 or 20 mv. on both sides of the equilibrium point, but the values for cathodic polarization then drop off, finally very rapidly. Equations 3 and 5 may be looked upon as representing the course of the reaction with low polarizations, but some superimposed effect is added at higher polarizations.

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[6] Van Laar, "Elektrochemie," Englemann, Leipzig, 1907, p. 158.

Table I

Experimental Data

ΔE, the potential, is given in millivolts; I, the current, in milliamperes. Anodic polarization is given the positive sign.

Expt. 80

0.1 N HCl. Bare electrode freshly activated

ΔE	− 0.95	*− 2.06	− 2.25	− 4.86	− 9.4	*− 9.6	−14.6
I	− 0.133	− 0.326	− 0.341	− 0.815	− 1.865	− 1.94	− 3.595
ka_{H_2}	0.00173	0.00186	0.00176	0.00176	0.00172	0.00173	0.00168
ΔE	−19.6	−25.0	+ 0.95	+ 2.42	*+ 2.58	+ 4.9	+10.3
I	− 5.80	− 8.67	+ 0.125	+ 0.338	+ 0.32	+ 0.58	+ 0.975
ka_{H_2}	0.00159	0.00142	0.00173	0.00195	0.00175	0.00182	0.00176
ΔE	*+10.9	+15.4	+21.4	....	....	....	....
I	+ 0.97	+ 1.22	+ 1.43	....	....	....	....
ka_{H_2}	0.00169	0.00174	0.00176	....	....	....	....

Expt. 75

0.1 N HCl. Bare electrode $3^1/_2$ hours after activation

ΔE	− 0.90	− 3.07	− 6.7	*− 6.8	−14.5	−24.5	−31.7
I	− 0.0751	− 0.0283	− 0.748	− 0.715	− 2.035	− 4.59	− 7.27
ka_{H_2}	0.00103	0.00104	0.00108	0.00102	0.0397	0.0379	0.0366
ΔE	−38.8	−48.8	+ 1.14	+ 2.02	*+ 2.24	+ 6.2	+10.6
I	−10.29	−15.45	+ 0.0913	+ 0.155	+ 0.1565	+ 0.41	+ 0.63
ka_{H_2}	0.0352	0.0331	0.00107	0.00107	0.0399	0.00107	0.00112

Expt. 76

0.1 N HCl. Same electrode as 75, 8 hrs. after activation

ΔE	− 2.07	− 3.84	*− 9.3	− 9.7	−20.1	*−33.6	−35.2
I	− 0.0755	− 0.151	− 0.398	− 0.446	− 1.207	− 2.69	− 3.09
ka_{H_2}	0.03429	0.03431	0.03372	0.03386	0.03314	0.03209	0.03211
ΔE	−50.0	−70.6	+ 1.17	+ 2.20	+ 3.93	+ 6.3	+10.2
I	− 6.00	−11.58	+ 0.0378	+ 0.0729	+ 0.120	+ 0.160	+ 0.235
ka_{H_2}	0.03122	0.0446	0.03432	0.03460	0.03454	0.03404	0.03415

Expt. 77

0.1 N HCl. Same electrode, 12 hours after activation

ΔE	− 1.46	− 3.54	− 7.02	−15.2	*−15.4	−30.2	*−49.9
I	− 0.0245	− 0.0632	− 0.140	− 0.390	− 0.390	− 1.112	− 2.89
ka_{H_2}	0.03203	0.03198	0.03191	0.03166	0.03167	0.03116	0.0461
ΔE	−50.1	−70.5	−92.2	+ 2.11	+ 5.56	+11.0	+19.7
I	− 2.88	− 5.60	− 9.80	+ 0.0325	+ 0.0785	+ 0.138	+ 0.200
ka_{H_2}	0.0458	0.04225	0.0572	0.03214	0.03224	0.03239	0.03254

Expt. 97

0.1 N HCl. Another series, 17 hours after activation

ΔE	− 8.1	−20.5	*−27.4	−27.5	−40.5	−50.3	....
I	− 0.0061	− 0.023	− 0.038	− 0.0375	− 0.0815	− 0.130	....
ka_{H_2}	0.0569	0.0559	0.0551	0.0550	0.0536	0.0527	....
ΔE	*−50.8	−60.6	−80.6	−98.7	....	....	....
I	− 0.158	− 0.194	− 0.356	− 0.591	....	....	....
ka_{H_2}	0.0531	0.05175	0.0668	0.0627	....	....	....

Expt. 85

1 N HCl. Immediately after activation

ΔE	− 0.38	− 0.97	− 2.0	− 5.0	−10.0	−19.5	−30.5
I	− 0.062	− 0.160	− 0.377	− 1.004	− 2.49	− 7.46	−19.45
ka_{H_2}	0.00207	0.00203	0.00223	0.00217	0.00209	0.00207	0.00197
ΔE	+ 0.85	+ 1.74	+ 4.8	+10.0	*+ 1.21	....	....
I	+ 0.15	+ 0.316	+ 0.715	+ 1.195	+ 0.188	....	....
ka_{H_2}	0.00233	0.00248	0.00228	0.00228	0.00209	....	....

Table I (*Continued*)

Expt. 86

1 *N* HCl. Same as 85, 3 hours after activation

ΔE	− 1.52	− 4.6	−10.4	−19.7	−30.0	−40.0	−50.0
I	− 0.073	− 0.243	− 0.611	− 1.512	− 3.175	− 5.54	− 9.35
ka_{H_2}	0.00058	0.0356	0.0348	0.0341	0.0334	0.0324	0.0319
ΔE	+ 1.58	*+ 4.75	+12.2	+21.0	....	....	....
I	+ 0.052	+ 0.125	+ 0.286	+ 0.38	....	....	....
ka_{H_2}	0.0344	0.0340	0.0347	0.0347	....	....	....

Expt. 91

0.1 *N* KOH. Plated electrode, fresh

ΔE	− 5.1	− 9.9	*−19.7	−19.8	−29.9	−40.2	−50.3
I	− 0.100	− 0.228	− 0.605	− 0.612	− 1.22	− 2.12	− 3.25
ka_{H_2}	0.03210	0.03197	0.03167	0.03166	0.03132	0.0497	0.0466
ΔE	+ 4.7	+11.0	*+16.5	+18.1	+27.8	....	....
I	+ 0.075	+ 0.175	+ 0.192	+ 0.203	+ 0.23	....	....
ka_{H_2}	0.03245	0.03305	0.03265	0.03269	0.03260	....	....

Expt. 93

0.1 *N* KOH. Plated electrode, aged

ΔE	− 5.8	−11.2	−19.3	−30.3	*−31.6	−39.0	−51.3
I	− 0.014	− 0.0326	− 0.072	− 0.164	− 0.172	− 0.275	− 0.519
ka_{H_2}	0.04246	0.04234	0.04206	0.04172	0.04166	0.04139	0.0598
ΔE	−59.4	−79.4	−100.7	+ 6.0	+14.0	+16.9	....
I	− 0.739	− 1.49	− 2.75	+ 0.0085	0.0175	0.0196	....
ka_{H_2}	0.0573	0.0531	0.0511	0.04228	0.04264	0.04268	....

Certain conclusions as to the mechanism of the reaction may be drawn from the validity of Equation 5 at low polarizations. The velocity with which hydrogen is oxidized is independent of potential (Equation 3*a*); the increase in the apparent velocity of the reaction on anodic polarization is due to the slowing down of the reverse reaction. The velocity of the reduction of hydrogen ion is bimolecular with respect to electricity and presumably with respect to hydrogen ion (3b). These conclusions are in accord with the hypothesis first put forward by Tafel[7] that the reaction proceeds in two steps; a rapid discharge of ions to form hydrogen atoms, and a slow combination to the molecular state, and similarly in reverse order for the reverse reaction. Potential variations will produce an effect only by varying the concentration of free atoms and hence the velocity of their combination, but will have no effect upon the velocity of the dissociation of the molecules.

Haber and Russ[4] in their work on the polarization of the quinone-hydroquinone electrode made the assumption of an intermediate active form of hydrogen as the reducing agent, and thereby arrived at an equation exactly analogous to Equation 5. Such an equation, $\Delta E = -0.074 \log \left(1 - \frac{I}{0.52}\right)$, is plotted as Curve C in Fig. 2, while the points represent the data of Russ[8] for the hydroquinone-quinone reaction on massive gold electrodes. The agreement is satisfactory for cathodic polarization, but the equation pre-

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[7] Tafel, *Z. physik. Chem.*, **34**, 200 (1900); **50**, 649 (1905).

[8] Russ, *ibid.*, **44**, 641 (1903).

dicts an entirely different course for the anodic polarization from that observed. The flattening off of Curve C on the anodic side is, however, a necessary result of the assumption of the intermediate hydrogen mechanism for the reaction. It is indeed possible to represent the positive polarization by another equation with reversed signs, as was done by Haber and Russ. Curve B is the function $\Delta E = 0.062 \log \left(\frac{I}{0.41} + 1\right)$. The positive values of B and the negative values of C do together represent the data, but no single equation is satisfactory.

The nature of the polarization curves observed by Haber and Russ suggests that the reaction velocities are expressible more nearly by equations analogous to 4 than by those of Type 3. A development similar to that of Equation 5 leads to the equation

$$I = 2k_2\, a_{H_2Q}\, e^{\frac{FE_0}{RT}}\ sinh\ \frac{F\Delta E}{RT}$$

(in place of $k_2 a_{H_2Q} e^{\frac{FE_0}{RT}}$ may be substituted $k_1 a_Q a^2_{H^+} e^{-\frac{FE_0}{RT}}$ or $\sqrt{k_1 k_2 a_{H_2Q} a_Q a^2_{H^+}}$)

which in the form $I = 0.66\ sinh\ \frac{F}{RT}\ \Delta E$ is plotted as Curve A in Fig. 2. The agreement is not perfect, and is indeed even worse with electrodes of lower catalytic activity, but it should be appreciated that the measurements were at a higher current density range than those of the present work on hydrogen. The theory of Equation 6 is certainly nearer the facts of the case than are the assumptions of Haber and Russ, and the intermediate hydrogen theory of such reactions should be abandoned as inadequate.[9]

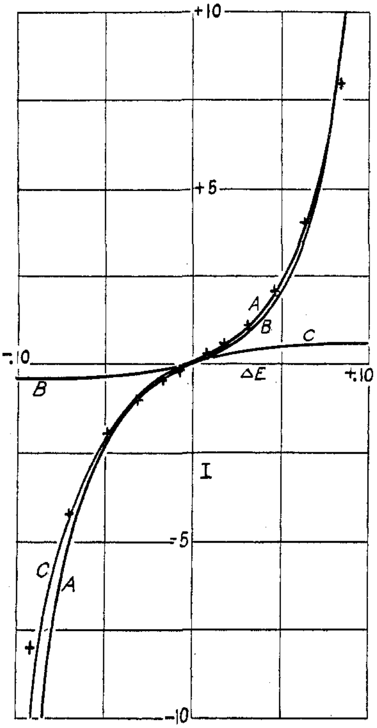

Fig. 2

It will be noted that the development of Equation 6 postulated nothing as to the mechanism of the reaction, which may therefore be considered to take place either directly by electron transfer, or by means of any suitable combination of successive reactions.

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[9] The work of Conant and Cutter, THIS JOURNAL, **44**, 2651 (1922), has an undoubted bearing upon this point, since non-reaction with such powerful reducing agents as chromous chloride is not in agreement with the hypothesis of a reactive atomic hydrogen, easily formed from hydrogen ion, as the active agent.

Table II

Current Ratios

80:75										
ΔE	-2.0	-5.0	-10.0	-15.0	-20.0	-25.0	+2.0	+5.0	+10.0	..
R	1.67	1.62	1.64	1.75	1.77	1.82	1.73	1.68	1.60	..
75:76										
ΔE	-3.0	-7.0	-15.0	-25.0	-32	-38	-48	+2.5	..	..
R	2.44	2.63	2.67	2.79	2.89	2.85	2.71	2.54	..	..
ΔE	+5.0	+7.5	+10.0	..	..	..	..	..	..	..
R	2.48	2.50	2.60	..	..	..	..	..	..	..
76:77										
ΔE	-2.5	-5	-10	-20	-35	-50	-70	+2.5	+5.0	+10.0
R	2.00	2.11	2.15	2.07	2.08	2.08	1.88	1.88	1.93	1.88
77:97										
ΔE	-8	-20	-30	-50	-70	-90	..	..	..	..
R	27	27	26	22	21	20	..	..	..	..
85:80										
ΔE	-2	-5	-10	-15	-20	-25	+2	+5	+7.5	+10
R	1.23	1.21	1.18	1.20	1.36	1.50	1.29	1.27	1.28	1.25
75:86										
ΔE	-2.5	-5.0	-7.0	-15	-25	-31	-39	-48	..	..
R	1.88	1.94	2.03	2.12	2.11	2.06	1.97	1.81	..	..
ΔE	+2.5	+5.0	+7.5	+10.0	..	..	..	..	..	..
R	2.32	2.23	2.27	2.33	..	..	..	..	..	..
91:77										
ΔE	-5	-10	-20	-30	-40	-50	+5	+10	+15	+20
R	1.05	1.06	1.05	1.10	1.14	1.12	1.10	1.10	1.09	1.10
93:97										
ΔE	-30	-40	-60	-80	-100	..	..	..	..	..
R	3.5	3.7	4.0	4.3	4.4	..	..	..	..	..

The theory here developed predicts that the current for a given value of E should increase with increased hydrogen pressure. Overvoltage as ordinarily understood represents the excess of voltage necessary to bring about the evolution of hydrogen gas at the electrode, a state of affairs which was deliberately avoided in the present experiments. The total of this excess voltage is the summation of two effects, that due to the slow chemical reaction discussed in this paper, plus the concentration polarization due to the hydrogen supersaturation necessary to form the gas phase. This latter effect has been treated by MacInnes and Adler[10] and shown to be decreased by increased pressure. There should, therefore, be no doubt that total overvoltage is decreased by increased pressure, as indeed appears from the experiments of Goodwin and Wilson,[11] although there are at present no data by which to apportion the relative importance of the chemical and of the concentration polarization.

By Equation 5, the polarization should be independent of the hydrogen-ion activity. In actual fact the effect is almost negligible except over such wide ranges as between strongly acid and alkaline solutions. It is of in-

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[10] MacInnes and Adler, This Journal, **41**, 194 (1919).

[11] Goodwin and Wilson, *Trans. Am. Electrochem. Soc.*, **40**, 173 (1921).

terest that Brunner[12] pointed out from the data of Tafel[7] that over voltage on mercury was roughly independent of the acid concentration.

There remains the consideration of the deviations from Equation 5. With regard to diffusion it may be pointed out that the range over which Equation 1 holds is much greater than the range over which Equation 5 is valid. As was pointed out by Haber, concentration polarization may be considered negligible as compared with chemical polarization over the range within which Equation 1 holds. The deviations from this equation in the present investigation are entirely in harmony with the supposition that the cause is concentration polarization. On comparison of two electrodes in the same acid there seems to be a tendency for the relative current on the more active electrode to drop off at the higher current densities; for different acid concentrations the relative current in the more dilute solution decreases at higher current densities, diffusion being slower because of the lower concentration of hydrogen ion. Moreover, the equation (a similar formula was developed by Brunner,[12])

$$I = \frac{k_2\, a_{\mathrm{H}_2}}{\left(1 + \frac{k_2}{D_2}\right)} \left\{ 1 - \left(1 + \frac{I}{D_1\, a_{\mathrm{H}^+}}\right)^2 e^{-\frac{2F\Delta E}{RT}} \right\} \tag{7}$$

where D_1 and D_2 are the diffusion coefficients of hydrogen ion and hydrogen, respectively, which may be obtained by combination of the well-known diffusion laws with Equation 3, is incapable of representing the experimental results. It may be concluded that diffusion exerts an effect only at high current densities and that some other effect is present in the range where Equation 1 holds but 5 does not.

In many cases[13] it has been possible to represent polarization curves by an expression of the form, $E = x(RT/nF)ln(I/k)$, where x is not necessarily an integral number greater than one. If the logarithm of the current in the present investigation be plotted against the potential the curve is not linear even at potentials at which the effect of the reverse reaction should be negligible. The curvature does, however, decrease as the polarization increases and it may be expected that for such polarizations as are encountered in the cathodic evolution of hydrogen on mercury the curve will be practically linear.[7,14] Haber's empirical equation is not therefore satisfactory in the range here studied.

The most satisfactory empirical equation for the present work is obtained by throwing Equation 5 into the logarithmic form, and adding a term representing a potential drop due to a resistance.

$$\Delta E = -\frac{RT}{2F}\, ln\left(1 - \frac{I}{k a_{\mathrm{H}_2}}\right) + rI \tag{8}$$

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[12] Brunner, *Z. physik. Chem.*, **58**, 1 (1907).

[13] See Haber, *ibid.*, **32**, 193 (1900), and Ref. 7.

[14] Lewis and Jackson, *ibid.*, **56**, 193 (1907).

In Table III is given a comparison of experimental data for Expt. 77 with this equation. The values, $ka_{H_2} = 0.00022$ and $r = 5.3$, were obtained by successive approximation. It is obvious that within the range of validity of Equation 1 this equation will also apply to all the other results, provided r be made inversely proportional to ka_{H_2}. It is, however, difficult to look upon this as indicating the existence of an actual ohmic resistance, such as the transfer resistance postulated by Newbery;[15] for a mechanism by which this resistance should be inversely proportional to the catalytic activity of the electrode is not easily imagined. The writer is inclined to regard Equation 8 as merely a convenient empirical equation.

TABLE III

EQUATION 8

I	−0.0245	−0.0632	−0.140	− 0.380	− 0.390	− 1.112	− 2.89	− 2.88	− 5.60	− 9.80
ΔE obs.	−1.46	−3.54	−7.02	−15.2	−15.4	−30.2	−49.9	−50.1	−70.5	− 92.2
ΔE calc.	−1.47	−3.55	−7.01	−14.8	−15.1	−28.9	−49.1	−49.1	−71.5	−100.7
% diff.	+0.7	+0.3	−0.14	− 2.6	− 1.9	− 4.2	− 1.6	− 2.0	+ 1.4	+ 9.2

The two deviations from the theory represented by the effect of hydrogen-ion activity upon the velocity of the reaction and by the decrease in the catalytic activity at high cathodic polarizations are in qualitative agreement in that a decrease in hydrogen-ion activity renders the electrode more negative. Quantitatively, however, a reduction of the acid concentration to one-tenth reduces the velocity of the reaction to 75% of its original value, while cathodic polarization of 50 mv. reduces the value of $k_2a_{H_2}$ to 34%. There may, therefore, be no connection between the mechanisms of the two deviations. It is unfortunate that the impossibility of satisfactory measurements at high anodic polarizations makes uncertain even the sign of the deviation for the positive side.

The writer is of the opinion that the deviations are to be ascribed to the fact that this is a surface reaction rather than to its electrochemical nature. The "Constant Sum Hypothesis" of Reichinstein[16] or Langmuir's theory[17] of heterogeneous catalysis may be adapted to explain qualitatively the deviations at high polarizations, but they do not explain the effect of hydrogen-ion activity, and the writer has been unable to develop a satisfactory quantitative theory based on these principles.

Summary

The polarization of the hydrogen-hydrogen ion reaction on platinum electrodes of a wide range of catalytic activity has been measured.

An equation has been developed on general grounds which represents the data satisfactorily for small polarizations.

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[15] Newbery, particularly *Trans. Faraday Soc.*, **15**, 126 (1919).

[16] Reichinstein, *Z. Elektrochem.*, **19**, 672; 914 (1913); **20**, 406 (1914); **21**, 360 (1915).

[17] Langmuir, THIS JOURNAL, **38**, 1143 (1916); **39**, 1848 (1917).

The results are in harmony with the hypothesis that the reaction proceeds in two stages; a rapid electrochemical reaction consisting in the discharge of hydrogen ions to atoms, followed by a much slower combination to form molecules, and similarly for the reverse reaction.

The deviations from the theoretical equation have been discussed and certain possible causes eliminated. An empirical equation to represent the data has been formulated.

The equation used by Haber and Russ to represent their results on the polarization of the quinone-hydroquinone electrode has been shown to be unsatisfactory in that it is incapable of giving both positive and negative polarizations with a single equation. A more satisfactory equation has been proposed, and it has been suggested that the intermediate hydrogen mechanism for the quinone reduction is incorrect.

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[Contribution from the Chemical Laboratory of the Ohio State University]

THE INFLUENCE OF GELATIN ON THE TRANSFERENCE NUMBERS OF HYDROCHLORIC ACID

By Wesley G. France and Walter H. Moran

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Introduction

In a previous article[1] by Alfred L. Ferguson in co-authorship with one of us it has been shown that gelatin in the presence of sulfuric acid results in an increase in the transference number of the anion. Over a concentration range of 0 to 20% of gelatin the anion transference number undergoes a change of from 0.187 to 0.685. As a result of these measurements together with conductivity measurements the opinion was expressed that "the action of gelatin and sulfuric acid results in the formation of a single dissociable product in which the H^+ ion loses its identity." It was with a view of substantiating this opinion that the present investigation of the influence of gelatin on the transference numbers of hydrochloric acid was undertaken.

Since the appearance of the above-mentioned paper, but two investigations of a similar nature have been published, one by Rene Audbert[2] who used gelatin in concentration cells of the type, AgI-$AgNO_3$, and found a lowering of the electromotive force which he explained as selective adsorption of the silver ion by the gelatin added; the other by J. W. Corran[3] who measured the influence of various concentrations of sucrose, 0 to 70%, on concentration cells of potassium chloride with and without transference.

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[1] Ferguson and France, This Journal, **43**, 2161 (1921).

[2] Audbert, *Compt. rend.*, **176**, 838 (1923).

[3] Corran, This Journal, **45**, 1627 (1923).