Code 2020 (2)

NRL REPORT 3877

FR-3877

ALKALINE STORAGE BATTERIES

FACTORS AFFECTING THE HYDROGEN EVOLUTION OF NICKEL-IRON BATTERIES WHILE STANDING CHARGED

NAVAL RESEARCH LABORATORY

WASHINGTON, D.C.

NRL REPORT 3877

ALKALINE STORAGE BATTERIES

FACTORS AFFECTING THE HYDROGEN EVOLUTION OF NICKEL-IRON BATTERIES WHILE STANDING CHARGED

A. L. Pitman

November 9, 1951

Approved by:

J. C. White, Head, Electrochemistry Branch
P. Borgstrom, Superintendent, Chemistry Division

NAVAL RESEARCH LABORATORY

CAPTAIN F. R. FURTH, USN, DIRECTOR

WASHINGTON, D.C.

DISTRIBUTION

CNO	1
ONR	
Attn: Code 425	2
BuShips	10
Attn: Code 560S	5
BuOrd	
Attn: Code Re6a	3
BuAer	
Attn: Mr. M. A. Knight, Code EL-501	2
CDR, USNOL	
Attn: Dr. A. G. Hellfritzsch	2
CO & Dir., USNEL	2
CDR, USNOTS	
Attn: Reports Unit	2
Wright-Patterson AFB	
Attn: BAU-CADO	1
Attn: CADO-E1	2
Attn: CADO-D13	1
Attn: Mr. W. A. Rose, AMC	2
OCSigO	
Attn: Ch. Eng. and Tech. Div., SIGTM-S	1
CG, SCEL	
Attn: SCEL Liaison Office	3
Attn: Mr. G. B. Ellis	2
Dir., NBS	
Attn: Dr. W. J. Hamer	2
Detroit Arsenal, Center Line, Michigan	
Attn: Mr. L. S. Gerber, Ordnance Dept.	2
Atomic Energy Commission, P.O. Box E, Oak Ridge, Tenn.	
Attn: Documents Control Branch, Technical Information Service	30
RDB	
Attn: Information Requirements Branch	2
Attn: Navy Secretary	1
Naval Res. Sec., Science Div., Library of Congress	
Attn: Mr. J. H. Heald	2

CONTENTS

ABSTRACT

The rate at which hydrogen is given off after a charge to a negative plate is ended consists of three additive parts: (a) evolution of hydrogen which had been dissolved in the active iron during charge—time, one hour; (b) evolution of hydrogen corresponding to the decline of negative potential to the stationary potential—time, about 15 minutes; (c) hydrogen evolution at an essentially constant negative plate potential. When oxygen is absent, this rate is proportional to the area of the iron surface which is not covered with corrosion product. Mathematical analysis of the data indicates that the latter consists of a constant number of growing hemispheres.

The stationary negative plate potential was found to be a logarithmic function of the activity (thermodynamic concentration) of water in the electrolyte in accordance with the Nernst equation for the equilibrium potential of the reaction:

$$Fe + 2H_2O = FeO_2H^- + H^+ + H_2.$$

The rates of formation of hydrogen upon periods of stand at 80° F for 1-13 hours were proportional to the square root of water activity of the electrolyte used. In the above time interval and per 1000 amperes of cell capacity (at normal rate) hydrogen evolution amounted to 11 liters if the electrolyte was at 1.2 sp gr; 9.3 liters at 1.3 sp gr; and 6.2 liters at 1.4 sp gr.

The capacity of a battery reached a maximum at 1.3 sp gr which was 15 percent above the capacities found at 1.2 and 1.4 sp gr.

PROBLEM STATUS

This is an interim report; work is continuing.

AUTHORIZATION

NRL Problem C05-09R
NR 405-090

Manuscript submitted August 22, 1951

ALKALINE STORAGE BATTERIES

FACTORS AFFECTING THE HYDROGEN EVOLUTION OF NICKEL-IRON BATTERIES WHILE STANDING CHARGED

INTRODUCTION

Hydrogen evolution from main submarine storage batteries during stand is limited by specification (1). "Hydrogen evolution for the total battery, on stand or discharge, shall not exceed 900 cubic feet in 48 hours with a battery average temperature of 100°F. The corresponding rate of hydrogen evolution per cell shall be inversely as the number of cells. Thus, if 780 cells are used, then the evolution shall not exceed 1.15 cubic feet in 48 hours per cell." This requirement cannot be met by an unmodified nickel-iron storage battery of the required capacity. The present work has been directed towards a study of various factors, particularly electrolyte concentration, affecting hydrogen evolution during a standing period after a normal charge.

It has been hypothesized that the initial rapid hydrogen evolution was due to the release of hydrogen which had been dissolved during charge in the negative active material (2). Most of the thinking about hydrogen evolution is conditioned by observations made on lead-acid cells where the first rapid rush of hydrogen has been ascribed to mechanically trapped gas. It has been known that hydrogen dissolves and penetrates into cathodically polarized iron plates (3). It is less generally known that the solubility of hydrogen in iron is roughly 200 times more than in lead under the same hydrogen pressure (4). Consequently, far more hydrogen will be dissolved and, later, evolved, from iron than from lead negative plate. The hydrogen desorption process from negative iron plates will be measured and discussed later.

Previous work (2) has shown that hydrogen is evolved on standing after a charge as follows:

$$\text{Total volume } H_2 \text{ (liters)} = B\,t^n + C \qquad (1)$$

where B, C, and n are constants in any one experiment. Constant B varies from battery to battery; C varies also with charging conditions. This equation is empirical except for the constant C which represents dissolved hydrogen. Up to the present, no logical equation has been advanced which also fits the data for 2000 or more hours as the empirical one does.

Increases in alkalinity above 1.2 sp gr (4.8 N) KOH in the electrolyte decrease hydrogen evolution on stand (1,5). At least two authors have stated that the life of nickel-iron batteries is less with higher concentrations than with 1.2 sp gr electrolyte (6). But no data on life tests at high electrolyte concentrations were presented by the authors nor have they been found elsewhere in the literature. Crennell and Lea (6) state that "with high concentrations [of electrolyte] the dangers due to the increased solubility of the iron in the electrolyte, particularly at high temperatures, become prominent, and

in practice, therefore, a slightly lower concentration than that which yields the maximum conductivity is employed." This reasoning is evidently conditioned upon the formation of the FeO_2H^- ion. Some workers (7) believed that the initial product is the FeO_2H^- ion, ferrous hydroxide being a secondary, cathodic product.

Marked reductions in hydrogen evolution on stand occur when more concentrated electrolytes are used (1,5). There is an apparent lack of complete knowledge of the reactions however, and this field has been abandoned by others (1). It was decided to study the corrosion rate of negative-charged plates and their potentials in relation to the effect of increasing concentration of alkali because such a study should aid in the solution of this problem.

EXPERIMENTATION AND OBSERVATIONS

Materials and Equipment

Nickel-iron storage batteries (275 A.H.) which were used in the past studies (8) were re-employed. When it became necessary to change the concentration of electrolyte, the cell was drained and refilled with an appropriate amount and concentration of potassium hydroxide (analytical grade). Fifteen grams of lithium hydroxide per liter were also present in the electrolyte. Specific gravities were checked after a cycle and the necessary adjustments were made. The Hg/HgO half cell, which was coupled through a modified electronic voltmeter to a Brown recorder, was used for measurement of the individual plate potentials. Direct readings of the half cell were also made against the negative plate by means of a Rubicon potentiometer. The gases evolved were measured and analyzed by the use of wet-test meters, Esterline-Angus impulse recorders, and Gow-Mac thermal conductivity cells. At the start of stands the meter was read at half-liter intervals for increased accuracy.

Correction of the Hydrogen Rate to That at the Negative Plate

Because of the head space in a storage battery, the concentration of hydrogen in the analyzed gas lags somewhat behind that corresponding to the time of evolution from the positive and negative plates. The hydrogen, together with oxygen from the positive plates, passes in part through a hydrogen analyzer cell, partly through a bypass; the two streams join and go through a wet-test meter. While there is no lag in the measurement of total volume, and thus of total rate, there is considerable lag in the recorded hydrogen concentration due to the presence of a liter or so of gaseous head space in a cell. To correct for this fact, a material balance of hydrogen was made. The input to the head space less the output from it equals the increase in hydrogen in that space. By this method it was possible to compute the hydrogen rate from the plates as if no head space were in the battery.

Hydrogen Evolution Rate in Relation to Time of Stand

It has been shown that on stand (1,2) of a fully charged negative plate in a Ni-Fe cell (275 A.H.), hydrogen is generated according to Equation (1), where C lies between 0.5 and 1.4 liters, and n is 0.67. This equation holds for over 3000 hours. The quantity C was indicated to be a correction factor representing dissolved hydrogen coming from the iron electrode upon release of the electrolytic pressure after the charging potential was cut off.

Partial and total hydrogen rates from the above cells are shown in Figure 1. The cells had been fully charged to theoretical gassing, using a normal rate at 80°F with an electrolyte of 1.2 sp gr. It was established by Platonova and Levina (5) and is now

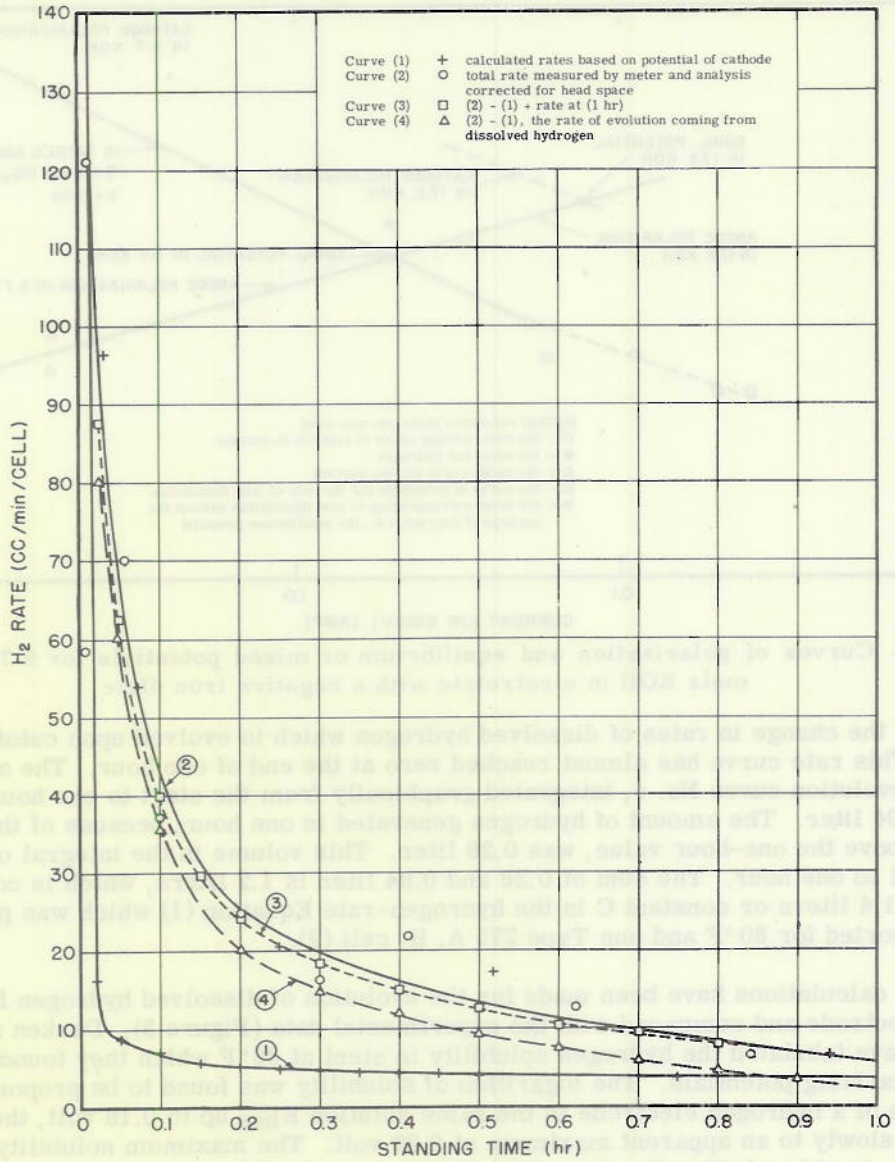

Figure 1 - Partial and total hydrogen rates

confirmed that the hydrogen rates generated upon cathode polarization for this system are equivalent to 100 percent of polarizing the current as read on the cathode polarization curve. This does not hold too closely, however, in the immediate vicinity of the equilibrium, or stationary, potential. The hydrogen rate for a Ni-Fe cell (275 A. H.) corresponding to a given potential above that of the stationary potential is the gas rate equivalent to the current read off from Figure 2. Curve No. 1 (Figure 1) represents the rate of hydrogen formation which was derived by means of the above relations from a cathode polarization curve (Figure 2) constructed for Ni-Fe cells (275 A. H.).

Curve No. 2 (Figure 1) gives the hydrogen rate as measured by gas meter and hydrogen analyzer cell, converted into rates, and then corrected for the presence of the head space. The rate of evolution which might be expected if the potential of the cathode had been maintained constant at its one-hour value is given by curve No. 3, which is No. 2 curve minus No. 1 curve plus the gas rate for hydrogen at one hour. In curve No. 4, the total corrected hydrogen rate from the cathode less that based on potential,

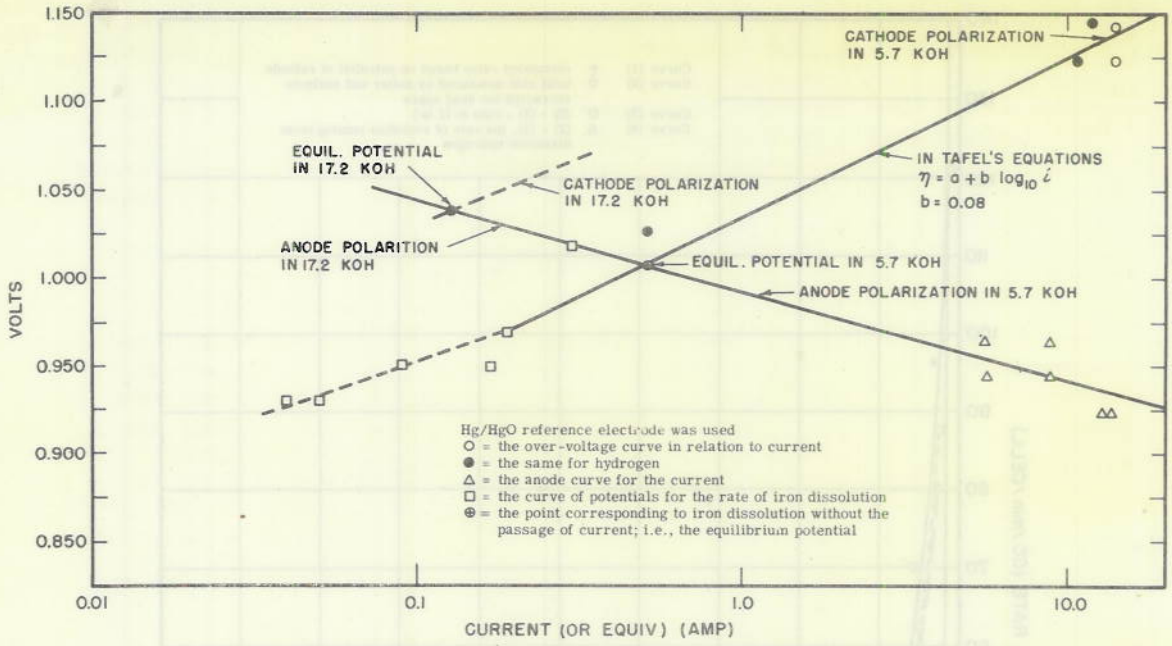

Figure 2 - Curves of polarization and equilibrium or mixed potentials for 5.7 and 17.2 mols KOH in electrolyte with a negative iron plate

represents the change in rates of dissolved hydrogen which is evolved upon cutoff of the current. This rate curve has almost reached zero at the end of one hour. The area under the evolution curve No. 4, integrated graphically from the start to one hour, is equal to 0.94 liter. The amount of hydrogen generated in one hour, because of the potential above the one-hour value, was 0.28 liter. This volume is the integral of curve No. 1 to one hour. The sum of 0.28 and 0.94 liter is 1.2 liters, which is comparable to 1.4 liters or constant C in the hydrogen-rate Equation (1) which was previously reported for 80 °F and one Type 275 A. H. cell (2).

Some calculations have been made for the evolution of dissolved hydrogen from the iron electrode and compared with the experimental data (Figure 3). Darken and Smith (9) have tabulated the hydrogen solubility in steel at 86°F which they found for various polarizing potentials. The logarithm of solubility was found to be proportional to the value of a hydrogen electrode in the same solution E_{hss} up to 0.18 volt, then it rose more slowly to an apparent maximum at 0.23 volt. The maximum solubility of hydrogen derived by plotting the data of Darken and Smith (9) is 0.25 cc at ntp per g of steel (Type S.A.E. 1020). For a fully charged negative iron plate in a Ni-Fe battery (275 A. H.) at 80°F and at a normal rate of charge, E_{hss} is 0.265 volt. The maximum solubility is therefore applicable to the present case. The negative plates in the above type of Ni-Fe cell weigh approximately 10 pounds which together with the maximum solubility gives 1.1 liters of hydrogen as the quantity which is dissolved in the negative plates when fully charged and still polarized. This amount is close to one liter, the graphical integral of rate curve No. 4 (Figure 1) which represents the same physical quantity. In computing the theoretical curve No. 2 (Figure 3) after the method of Gurney and Lurie (10), one liter has been used as the total amount of dissolved hydrogen.

It is well known among chemical engineering designers that the same fundamental differential equations of Fick apply both to heat transfer and the diffusion of substances. In the present case, the problem is one of gas diffusion in the nonsteady state. The publication of Gurney and Lurie (10) gives methods for handling heat conduction to or from variously shaped objects under nonsteady conditions. The objects were initially of a uniform temperature; then the external temperature was suddenly changed to a different, but constant one. It can be seen that if one assumes a certain shape for the

particles of active iron, the above method provides a tool whereby the dissolved hydrogen content in the negative iron plates can be related to the initial content of hydrogen at any time from the end of charge. The hydrogen evolved for any length of time will be one liter minus the calculated volume of remaining dissolved gas.

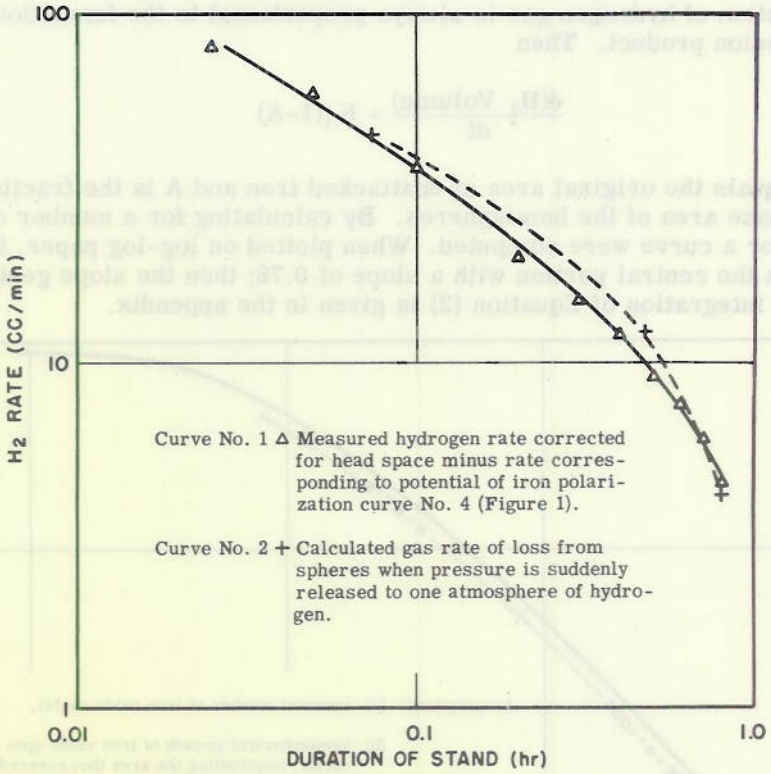

Figure 3 - Hydrogen rates on stand - 275 A. H. cells, charged at N rate, then to stand. 80°F and 1.2 sp gr electrolyte

A comparison of the calculated curve No. 2 (Figure 3) for the evolution of previously dissolved hydrogen with the experimental rate curve No. 1 (Figure 3) has been made. The data points for the latter curve were taken from curve No. 4 (Figure 1) and are thus on the basis of a constant potential on the surface of the iron plate. In Figure 3 the close fit of the calculated curve No. 2 to the experimental curve No. 1 is sufficient added evidence to prove that hydrogen is dissolved in measurable quantity in the negative plates during a charge and that it is evolved rapidly according to known diffusion laws when the charge is stopped.

It has been concluded by some writers (11) that the capacity of a negative iron electrode, and hence its ability to corrode, depends upon the gradual formation of a very thin film of an iron oxide. This surface oxide is said to constitute but a small percentage of the total reacting iron during a discharge (12).

It has been proposed by Evans (13) that the fraction of metal left uncovered by corrosion products may be equal to e^{-kt^2} if the corrosion spreads in circles, as from rain drops, at constant radial velocity. This is a film-like growth in two dimensions from an initial random distribution of nuclei, the number of which is constant with time. Lander (14) has suggested that in general corrosion may be limited by the proportion of untouched area of metal; but the corrosion product was assumed to be three-dimensional with a constant number of nuclei.

Calculations have been made for the integral of a hydrogen rate curve assuming that: (a) the solid corrosion product builds upon a fixed number of crystal centers; (b) the iron products of corrosion form hemispheres upon spreading circular bases of a surface oxide film; (c) the rate of attack is proportional to the remaining uncovered iron surface area; (d) the cathode potential is constant; and (e) the chemical formation and subsequent evolution of hydrogen gas is always proportional to the formation of the solid-iron-corrosion product. Then

$$\frac{d(H_2 \text{ Volume})}{dt} = K_1(1-A) \qquad (2)$$

in which unity equals the original area of unattacked iron and A is the fraction of iron covered by the base area of the hemispheres. By calculating for a number of increments of time, points for a curve were computed. When plotted on log-log paper, the curve is roughly linear in the central portion with a slope of 0.78; then the slope gently decreases (Figure 4). The integration of Equation (2) is given in the appendix.

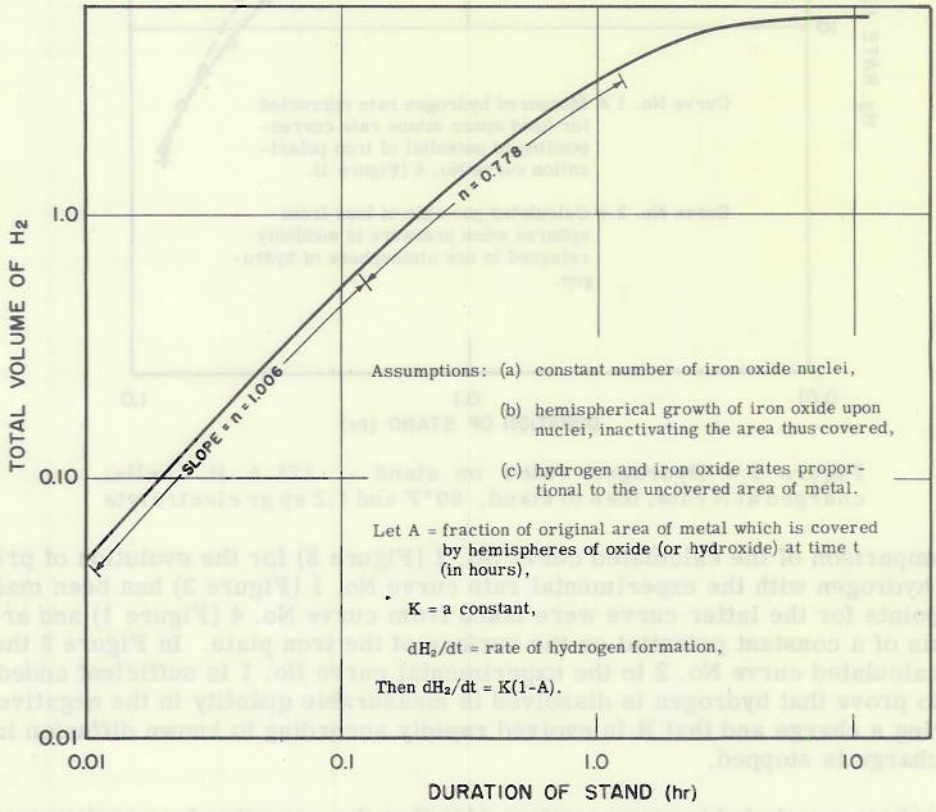

Figure 4 - Theoretical hydrogen evolution if the rate is proportional to the uncovered area of metal

In the graphical integral of Equation (2) (Figure 4) no units are expressed for hydrogen or time since the derivation did not include such units. An assignment of units to the ordinates and abscissas merely translates the theoretical curve parallel to the coordinates but does not rotate the curve. Data from a stand with pure iron powder in Ni-Fe refill electrolyte, and in the absence of air (15), were plotted (Figure 5) on transparent log-log paper with the same cycle dimensions as in Figure 4. Then the theoretically calculated curve (Figure 4) was placed beneath the experimental data (Figure 5) and the relative positions were adjusted in a rectilinear fashion to achieve the best match; then the theoretical curve of Figure 4 was traced upon Figure 5. The agreement of the calculated curve with experimental data is almost perfect.

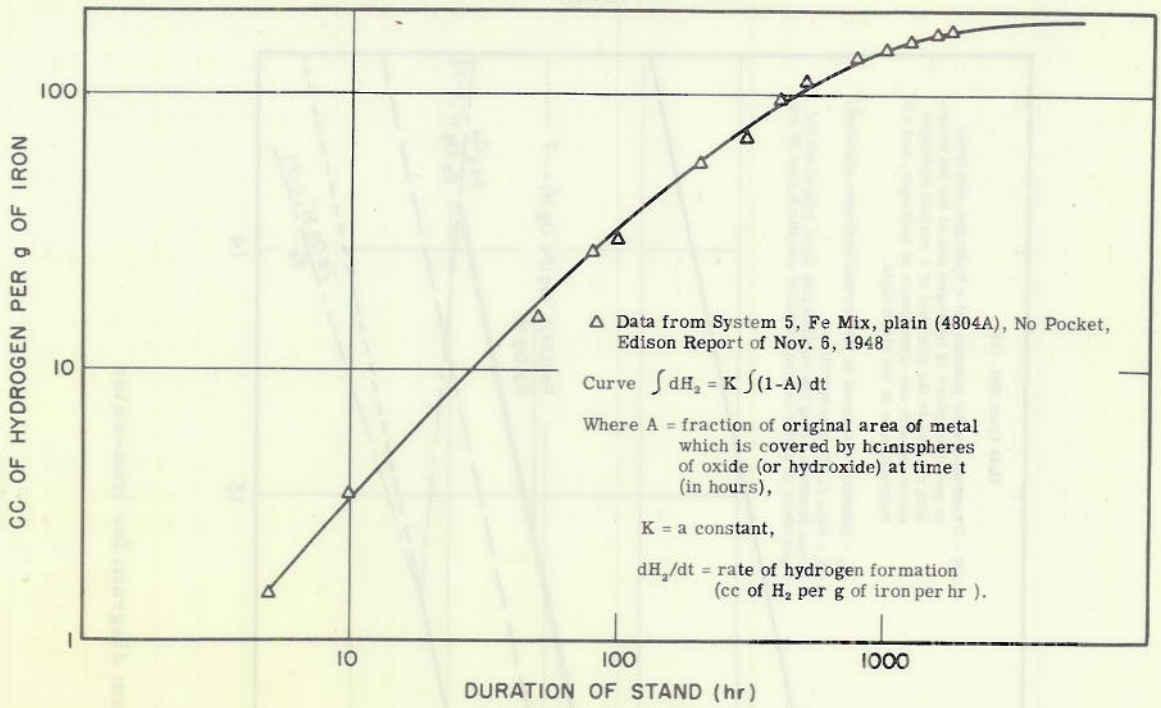

Figure 5 - Hydrogen evolution from isolated negative plates

Schikorr's data (16) for iron-water in the absence of air shows on a log-log plot a tendency to approach zero slope in a manner analogous to the theoretical and experimental curves in Figure 5. Evidently a rational explanation has been found for the relation between hydrogen evolution and time in long stands when oxygen is absent.

The explanation, embodied in Equation (2), states that the corrosion rate is controlled quite completely by the ratio of iron area as yet uncovered by corrosion products. This area can serve for both anode and cathode area so far as the postulates of Equation (2) are concerned. That is, this equation is consistent with the Wagner-Traud theory of mixed potentials (17).

Equilibrium Potential in Relation to the Electrolyte Concentration

In strongly alkaline solutions iron is attacked and converted at some stage to a form in which it is in the negative ion. Pourbaix (18) has gathered together data on the potential versus pH diagram of iron-water, part of which is presented in Figure 6. Working in more dilute solutions than 1.2 sp gr of KOH, Randall and Frandsen (19) found for the reaction

$$Fe + 2\,OH^- = Fe(OH)_2 + 2e \qquad (3)$$

a standard potential of 0.877 volt as compared to the normal hydrogen electrode, or 0.045 volt as compared to a reversible hydrogen electrode in the same solution. Using an iron powder which had been formed from precipitated hydroxide, reduced, dried, and compressed within perforated plates, Platonova and Levina (5) investigated the electrolytic behavior of iron in 4.8 N and 10.5 N KOH. They concluded that the stationary potential with respect to a hydrogen electrode in the same solution was essentially equal to 0.045 volt. The stationary potential is that potential limit which is reached by the negative plate with decreasing polarization current. They believed that they had confirmed the above reaction (3) as correct under their conditions.

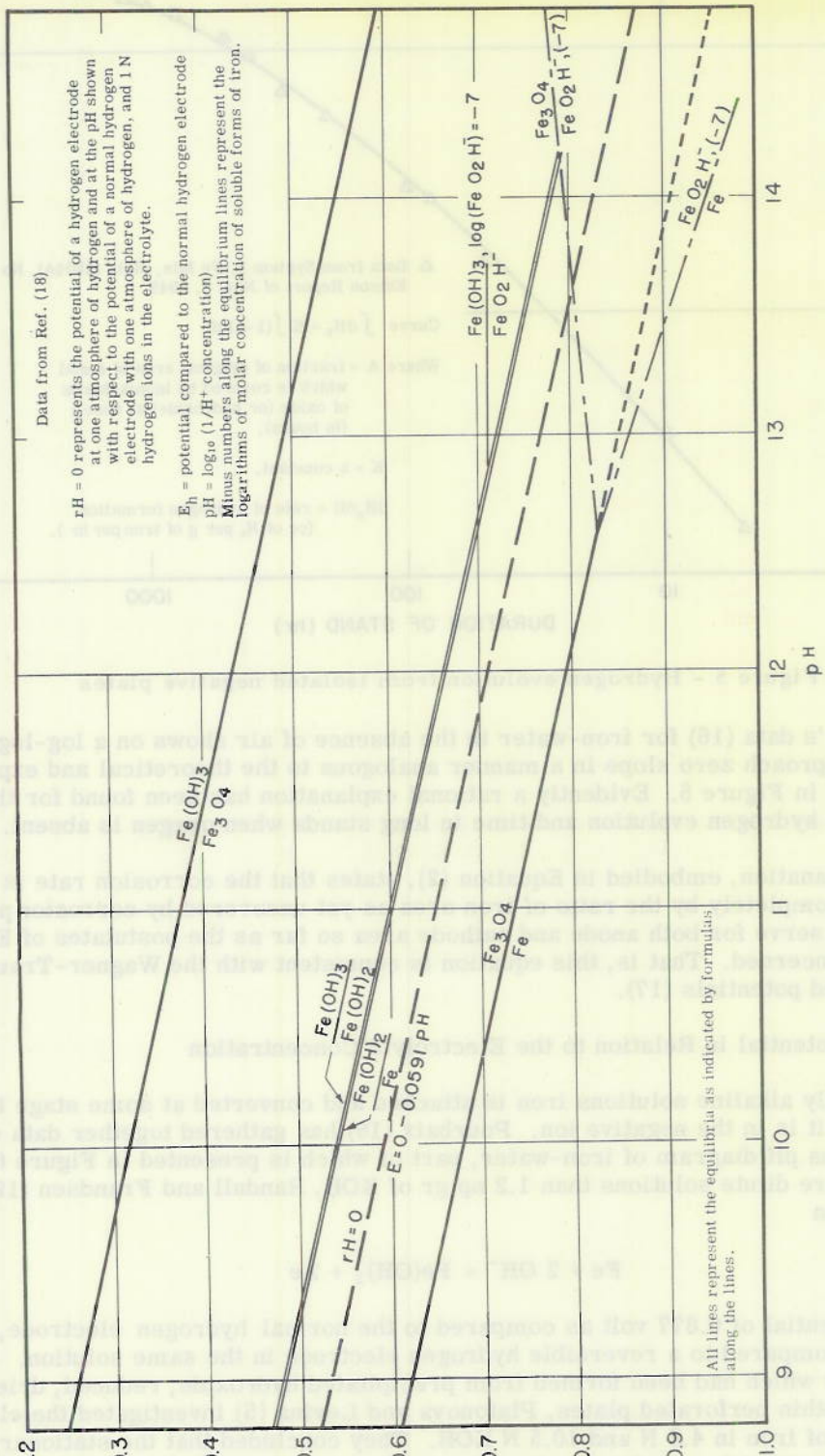

Figure 6 - Potential versus pH equilibrium diagram for iron-water

A year earlier Kabanov and Leikis (7) found that in a 2 N NaOH an iron anode process at 0.050 volt and a iron cathode process at 0.13 volt compared to the hydrogen electrode in the same solution. They concluded that the first anodic process is the formation of $Fe(OH)_2$ from iron. Then from the solubility product $(FeO_2H^-)/(OH^-) = 2.5 \times 10^{-5}$ mol per liter as given by Schrager (20), the complex ion, FeO_2H^-, is stated to be an intermediate product before the hydroxide (7).

The foregoing references are not in complete agreement upon the mechanism of the attack which iron undergoes upon a stand in strong alkaline solution. In an attempt to clarify the various results and conclusions, part of the thermodynamic system for iron-water was computed in detail for the range of pH 9 to 14.8 using the equations given by Pourbaix (18). Various assumptions were then made for the solubility of the complex ion, FeO_2H^-. Figure 5 shows the data with the complex ion at 10^{-7} mol per liter. This concentration was selected because it was found that at pH 14.2, representing 2 N NaOH, the process Fe/FeO_2H^- corresponded to +0.13 volt which was relative to the hydrogen electrode in the same solution, E_{hss}. The other polarization process corresponded to FeO_2H^-/Fe_3O_4 at -0.05 volt. Figure 6 shows that the line representing this latter process and the line for the $Fe/Fe(OH)_2$ potential when extrapolated to pH 14.2 have the same value. Pourbaix (18) has pointed out that magnetite is stable in a region which entirely covers the region of stability determined for ferrous hydroxide. It is, therefore, considered probable that the equilibrium of iron when polarized negative to the hydrogen electrode may represent the couple FeO_2H^- ion/Fe_3O_4.

In either electrode process, water is one of the reactants. Accordingly, since the variation of the concentration of reactants is one method of investigating reactions from an equilibrium, as well as kinetic view-point, the potentials of the negative plate and the rates of hydrogen evolution for a given length of standing time were measured at different electrolyte concentrations. Table 1 gives the results for hydrogen evolution. By setting Y' equal to the number of liters of hydrogen evolved from 1 to 13 hours and X equal to the specific gravity of the electrolyte, the following equation was derived by the least square method:

$$Y' = 11.970 - 7.248\ X. \tag{4}$$

A statistical "t" test has been made to determine the reliability of the slope in Equation (4). The chances are slight (probability of 0.05) that the slope of the line defined by Equation (4) differs more than 12 percent from the value in the equation.

It is proposed to use the equilibrium data derived from hydrogen evolution rates in relation to electrolyte concentration to decide whether the process is according to Equation (3) or is

$$Fe + 2\ H_2O = FeO_2H^- + H^+ + H_2. \tag{5}$$

For Equation (5) the anodic reaction may be written

$$Fe + 2\ OH^- = FeO_2H^- + H^+ + 2e \tag{6}$$

and the cathodic reaction is

$$2\ H_2O + 2e = H_2 + 2\ OH^-. \tag{7}$$

or

$$H_2O + e = 1/2\ H_2 + OH^-. \tag{8}$$

Let E_{hss} represent the potential with respect to the hydrogen electrode in the same solution under experiment; E_a, the anode potential; E_c the cathode potential; E^0 the standard potential. Thermodynamic concentrations are expressed as activities and R, T, and F have the usual meanings. Further, a_{H_2O} is the activity of water; $a_{FeO_2H^-}$, the activity of the indicated ion; P_{H_2}, hydrogen pressure; a_{H^+}, the activity of that ion. Then the

TABLE 1
A Comparison of the Hydrogen Evolutions from Negative Iron Plates upon Stands in Relation to the Specific Gravity of the Electrolytes. (Nickel-Iron Cells, 275 A. H.)

Specific Gravity	Hydrogen Evolved (in liters)			Room Temp (°F)
	To 1 hr	To 13 hr	From 1-13 hr	
1.2	1.60	5.30	3.70	
	1.10	3.60	2.50	
	1.60	5.20	3.60	
	1.20	3.80	2.60	
	1.40	4.40	3.00	
			3.1 av.	
1.3	1.35	3.67	2.32	79.5
	1.50	4.37	2.77	78.2
	1.40	4.00	2.60	
	1.75	4.25	2.50	81.0
	1.40	3.35	1.95	78.9
	1.25	3.75	2.50	77.9
	1.30	4.10	2.80	81
			2.5 av.	
1.4	1.75	4.15	2.40	78.0
	1.55	4.00	2.45	81.2
	1.35	4.25	2.90	78.1
	1.10	3.75	2.65	81.2
	1.35	2.50	1.15	79.0
	1.75	3.15	1.40	79.0
	1.62	3.40	1.78	79.3
	1.90	3.90	2.00	79.3
			2.1 av.	
1.48	1.30	2.40	1.10	77.8
	1.65	2.70	1.05	77.8
	2.15	3.25	1.10	79.2
	2.30	3.40	1.10	79.9
			1.1 av.	

Nernst equation for Equation (5) is

$$E_{hss} = E_a^o - E_c^o + \frac{RT}{2F} \ln \frac{(a_{H_2O})^2}{a_{FeO_2H^-} (P_{H_2})\, a_{H^+}} \qquad (9)$$

and

$$(a_{H^+})\,(a_{OH^-}) \,/\, (a_{H_2O}) = 1.005 \times 10^{-14} \,. \qquad (10)$$

Substitution of the values for the activities of FeO_2H^- and of hydroxyl ion leads to an expression free of indeterminate, or difficulty measured, factors.

$$E_{hss} = E^o + \frac{RT}{2F} \ln \frac{a_{H_2O}}{P_{H_2}} \qquad (11)$$

In Equation (11), P_{H_2} is the pressure of hydrogen in atmospheres. For a constant pressure of hydrogen, the difference in the E_{hss} which would arise if two cells with

different concentrations of electrolyte were compared would be

$$\Delta E = \frac{RT}{2F} \ln \frac{(aH_2O)_2}{(aH_2O)_1} = \frac{RT}{F} \ln \frac{(aH_2O)_2^{1/2}}{(aH_2O)_1^{1/2}} \quad (12)$$

Thus, changes in the stationary potential of Equation (5) can be calculated for changes in electrolyte concentration if the activity of the water is known under those conditions. Fortunately a recent study (21) provides the needed data on water activity. In Table 2 data on hydrogen evolution are presented in relation to the electrolyte concentrations with respect to mols of KOH per 1000 g of water, to the activity of water, its square root, and finally a column is given over to the ratio of liters of hydrogen to the square root of water activity.

TABLE 2
Hydrogen Evolution in Relation to Electrolyte

H_2 (in l)*	Sp gr 80°/80°F	Mols KOH/ 1000 g H_2O	a_{H_2O}	$a_{H_2O}^{1/2}$	H_2 (in l)/$a_{H_2O}^{1/2}$
3.25	1.2	4.85	0.608	0.78	4.17
2.55	1.3	8.00	0.391	0.625	4.08
1.82	1.4	12.45	0.196	0.442	4.12
1.47	1.45	13.5	0.145	0.381	3.86
1.10	1.50	16.0	0.099	0.297	3.71

*Computed from column No. 2 using Equation (4).

The maximum variation of this ratio is 11 percent and the standard deviation is 0.185, or 5 percent of the ratio. It is concluded that the hydrogen evolution rate is proportional to the square root of the activity of water in the electrolyte. The consistency of the ratios of the hydrogen rate to the square root of water activity is shown in Figure 7.

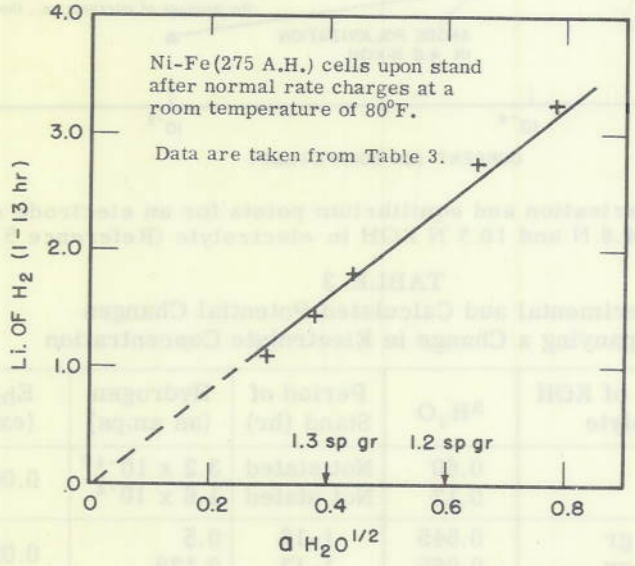

Figure 7 - Relationship between the hydrogen evolution rate and the square root of the activity of water in the electrolyte

Theoretical changes in the equilibrium potential may be compared with experimental ones through the use of polarization curves. In the preparation of polarization curves, an iron electrode, i.e., the negative plate group of a Ni-Fe battery in this study, was

connected to a motor generator as an external source of potential then back to the positive battery plates (in the present case). It will be recognized that the iron plates may be cathodically or anodically polarized at various current densities depending upon the polarity and extent of the external emf. That is, cathodic polarization, or charge, and anodic polarization, or discharge, of the iron electrode may be effected.

In comparing changes in actual equilibrium potential with the theoretical, use will be made of polarization curves of Platonova and Levina (5) on Figure 8 and curves from this study on Figure 2. Both of these figures show iron potential versus log current density; and the stationary, or equilibrium, potential has been shown at the intersection of the cathode and anode polarization lines. These stationary potentials are the experimental values compared to the Hg/HgO half cells after correction to the basis of a hydrogen electrode in the less concentrated solution. Actually in such strongly alkaline electrolytes as those indicated in Figures 2 and 8, the reference electrode is really the couple Hg/HgO_2H^- (22). Its potential change with alkaline concentration is theoretically equal to the change for the couple Fe/FeO_2H^-. Experimentally, too, the potential of Fe/FeO_2H^- versus Hg/HgO_2H^-, the actual reference electrode, does not change with the electrolyte concentration. But the potential of Hg/HgO_2H^- compared to a hydrogen electrode at a fixed alklalinity of electrolyte does change, so a correction of the potential is made because of this fact. Potentials plotted on Figures 2 and 8 are relative to the hydrogen electrode in the weaker solution investigated. In Table 3 are given the experimental and calculated ΔE's, the latter being computed by Equation (12). The agreement which the calculated values show with the experimental ones is added evidence that iron in strong alkalies is in equilibrium with the FeO_2H^- ion rather than with ferrous hydroxide.

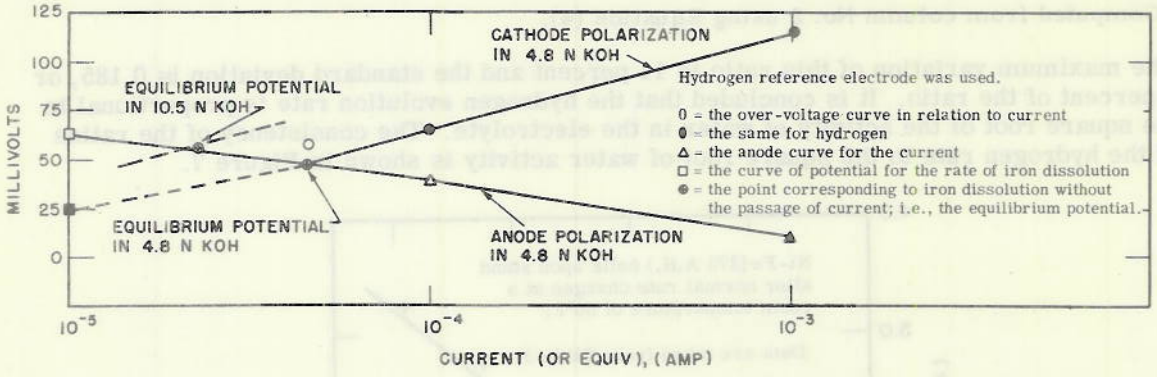

Figure 8 - Curves of polarization and equilibrium points for an electrode of pressed iron powder in 4.8 N and 10.5 N KOH in electrolyte (Reference 5)

TABLE 3
Experimental and Calculated Potential Changes
Accompanying a Change in Electrolyte Concentration

Data	Concentration of KOH in Electrolyte	a_{H_2O}	Period of Stand (hr)	Hydrogen (as amps)	Ehss (exp)	Ehss (calcd)
Ref (5)	4.8 N 10.5 N	0.60 0.17	Not stated Not stated	3.2×10^{-4}* 1.6×10^{-4}	0.009	0.010
NRL**	1.22 sp gr 1.53 sp gr	0.545 0.065	1-13 1-13	0.5 0.129	0.027	0.027
	1.22 sp gr 1.53 sp gr	0.545 0.065	1-13 1-13	0.54 0.129	0.032	0.027

* Apparent current density as amperes per sq cm
**Hydrogen rate from one Ni-Fe cell 275 A. H. as amperes

The Influence of Electrolyte Concentration upon Capacity

Ampere-hour capacities at normal rates of discharge in relation to the specific gravity of the electrolyte are shown in Figure 9. The maximum capacity is at 1.3 which is the same as in the Friemann-Wolf storage battery, an alkaline nickel-cadmium type (23). This latter data of Schmidt and Piening has been abstracted before (2).

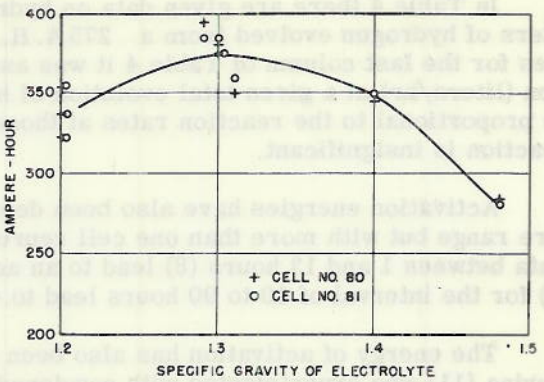

Figure 9 - Edison cells (275 A. H.) 80 °F, dependence of capacity (normal rate) upon specific gravity of electrolyte

The capacity of a Ni-Fe battery upon standing up to several hundred hours is determined by the capacity of its positive plates (8); it is conjectured that the same is true in the Friemann-Wolf battery. If so, the relationship in question is really between the capacity of the positive plates and the specific gravity of the electrolyte in both instances. Therefore the same maximum might well be expected in both cases. The normal capacity of a Ni-Fe battery (Type 275 A.H.) is 15 percent higher at 1.3 specific gravity than at 1.2, which is the standard specific gravity.

The capacity of the investigated Ni-Fe batteries, when operated with electrolyte above 1.3 sp gr, dropped more rapidly with increased concentration than did the capacity of the Friemann-Wolf battery.

Activation Energies for the Hydrogen Evolution Reaction

As pointed out first by van't Hoff, the influence of temperature upon an equilibrium constant can be expressed quantitatively by the equation

$$d(\ln K)/dt = Q/RT^2 \qquad (13)$$

in which K is the equilibrium constant, Q is the quantity of heat absorbed per mol, R is 1.99 g cal/ degree C / equivalent, and T is the absolute temperature (°Kelvin).

Arrhenius showed for "irreversible" reactions at different temperatures:

$$\log_{10} k_2/k_1 = A(1/T_2 - 1/T_1) \qquad (14)$$

where A is the activation energy per mol, k_1 is the forward velocity constant, and k_2 is the backward velocity constant.

TABLE 4
Total Hydrogen, Rates of Evolution, and Activation Energies

Temp (°F)	Total Hydrogen (l)	Hydrogen Rate (l/hr)	(Q kg cal)
100	10	0.33	5.72
80	10	0.235	
100	15	0.27	5.92
80	15	0.19	
100	20	0.235	5.95
80	20	0.165	

In Table 4 there are given data on hydrogen rates at 80° and 100°F at 10, 15, and 20 liters of hydrogen evolved from a 275 A. H. Ni-Fe cell. In computing activation energies for the last column of Table 4 it was assumed: (a) that the rates of hydrogen evolution (liters/hr) at a given total evolution of hydrogen but at different temperatures will be proportional to the reaction rates at those temperatures; (b) the rate of the reverse reaction is insignificant.

Activation energies have also been determined in this Laboratory in this temperature range but with more than one cell represented and with different ranges of time. Data between 1 and 13 hours (8) lead to an activation energy of 9400 g cals. Other data (2) for the interval of 10 to 90 hours lead to 4600 g cals.

The energy of activation has also been computed from the data of Kalmykova and Levina (11) who experimented with powdered iron at -30° and 20°C and at 1.28 to 1.30 sp gr of KOH.

Let I_0 represent the current density on a cathode polarization curve, as in Figures 2 and 8, at the equilibrium potential. Let A represent the activation energy, while R and T have their usual meanings. Then for the equilibrium potential

$$\log I_0 = \text{constant} - \frac{A}{2.3\,RT}. \qquad (15)$$

If data from Figure 1 of Reference (11) is used, the activation energy equals 7200 g cal for powdered iron. Other data of Kalmykova and Levina (11) for smooth iron gave an activation energy of 6000 g cal. A weighted average for all of the data given on powdered iron is 6800 g cal.

According to Glasstone (24) other experimenters, also working with alkaline solutions, found energy values similar to those given in Table 5.

TABLE 5
Activation Energies for Hydrogen Overvoltage
Using 0.2 N NaOH Electrolytes

Cathode	Activation Energy (kg cal)	I_0 (amp/cm^2)
Mercury	8.7	7×10^{-9}
Smooth Platinum	about 6.5	about 1×10^{-6}
Palladium	10.0	1×10^{-5}

Hydrogen Diffusion through Metal in Relation to Overvoltage

The relatively small effect of temperature changes upon rate has already lead to the suggestion (2) that the rate of hydrogen evolution may be diffusion-controlled. Two types of diffusion process suggest themselves: (a) diffusion of water through a stagnant film next to the iron electrode; (b) diffusion of atomic hydrogen on or through the iron metal electrode. The concept of diffusion is the basic idea. Data are given in Table 6 for the diffusion of heavy water. The diffusion constant for heavy water into water differs by little from that of water itself into water (25).

When the experimentally determined activation energy for the hydrogen-producing process of a charged negative plate placed upon stand are compared with the activation energies for the diffusion of hydrogen in different forms of iron, it is seen that the energy for the electrode process lies between the energies required for the diffusion of hydrogen in alpha- and in gamma-iron. The type of iron which is present in a cycling

TABLE 6
Diffusion of Heavy Water into Water
$D^* = D^0 e^{-E/RT}$

D (cm^2/sec)	Temp (°C)	E (kg cal)	Ref
1.1×10^{-5} 2.5×10^{-5}	0 28	4.6	(26)
1.46×10^{-5} 4.75×10^{-5}	0 45	5.3	(25)

*All available published data on diffusion constants and heats of activation for hydrogen-metal systems are collected in Table 7. These constants are presumably free from any resistance effect of surface films. Permeability constants, which are more commonly measured, do include such effects, however, where D is the diffusion constant, D^0 is a constant, E is activation energy, and R, T have the usual meanings.

TABLE 7
Diffusion of Hydrogen through Metals

System	D^0 (cm^2/sec)	D^* (cm^2/sec)	Temp Range (°C)	E (kg cal)	Ref
H-αFe		1.6×10^{-5}		2.90	(27)
H-γFe		5.4×10^{-10}		9.95	(27)
H- Fe	1.65×10^{-2}	2.5×10^{-9}	10-100	9.20	(28)
H-Pd	1.5×10^{-2}	1.5×10^{-7}		6.80	(29)
H-Ni	2.04×10^{-3}	9.5×10^{-10}	85-165	8.70	(30)

*See footnote for Table 6

negative electrode is not known. Alpha-iron is the normal stable form at room temperature. Insofar as activation energy may be used as a criterion, the rate-controlling process for the attack of iron with concurrent evolution of hydrogen could be a function of hydrogen diffusional processes.

DISCUSSION

It has been shown that the evolution of hydrogen from a charged iron plate suddenly cut off from charging consists of three separate processes: (a) evolution corresponding to the declining negative potential (essentially complete in 15 minutes), (b) desorption of dissolved hydrogen from the active metal, (c) corrosion of iron by water with the evolution of hydrogen.

The decay of the lead-acid-cell negative-plate potential, after a full charge is stopped, takes place in about 5 seconds (31) instead of the 15 minutes required for an iron-charged negative plate in alkaline solution (Figure 10). That is, an essentially stationary potential is reached in one-two hundredth the time that was observed for an iron plate. It is believed that this relationship is a function of the solubility and diffusion constant of hydrogen for each metal. Mellor (4) cites data of G. Neumann and F. Streintz (1892) in which one volume of powdered iron dissolved 19.2 volumes of hydrogen, while a corresponding volume of lead dissolved but 0.1 volume (one-190th as much). It has recently been discovered that the evolution of hydrogen from nickel cathodes continues

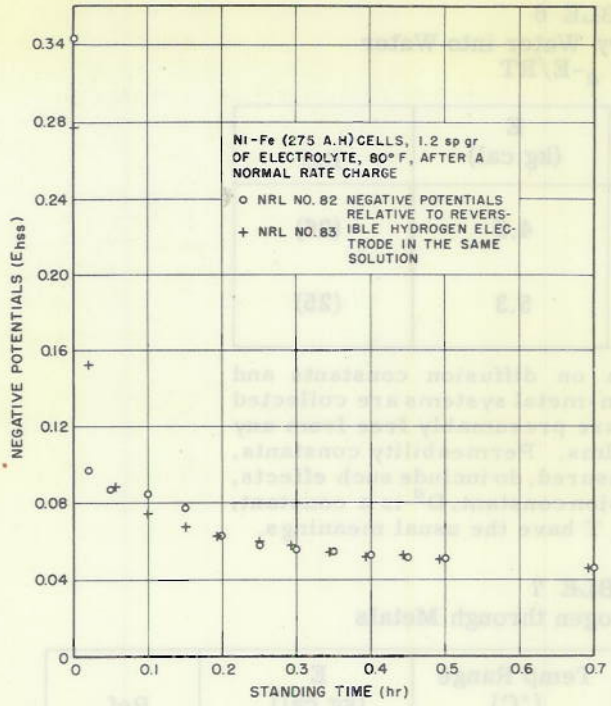

Figure 10 - Negative plate potentials with reference to standing time

for several seconds after the polarizing current is stopped if the latter is above 10^{-3} amperes per sq cm (32). It is suggested that the shapes of the potential decay curves for these three metals, caused by opening the cathodic polarizing current circuits, are certainly due in part to the desorption of dissolved hydrogen.

The corrosion of iron by alkaline solutions proceeds at a rate which is proportional to the remaining area of bare metal. A striking match of the theoretical and actual hydrogen evolution curves was found in isolated cathodes in the absence of oxygen. But under cell conditions, analyses indicated that perhaps 3 percent of oxygen is the minimum concentration in issuing cell gas during a long period of stand. Equations for hydrogen evolution derived from measurements on the gases from a whole cell indicate a slower evolution of hydrogen with time than when oxygen is absent but do not show the same tendency to cut off on extremely long stands. No explanation of this difference can be given as yet.

It is now regarded as established that an electrolyte of 1.3 sp gr will yield 15 percent higher capacity (amp hr) than at 1.2 sp gr. There are conditions where such an increase in capacity would be of real interest. But it has been stated (33) that higher specific gravities could not be used because of the known harm to battery life. No data on this point appears to have been published. Our experience only extends through a limited number of cycles. After operating at higher concentrations, one cell was refilled with 1.2 sp gr of electrolyte and still displayed its normal capacity. Two cells used at higher concentrations showed a black suspension, which of course, while indicative of a different behavior than at 1.2 sp gr, does not prove anything concerning life expectancy.

It has been shown that iron goes into a negative ion in all of these solutions. Such an ion will migrate towards the anode during parts of the cycle. Will more FeO_2H^- ions migrate when the electrolyte is stronger and, if so, how much would this condition shorten the life of the battery? On the other hand, if migration is limited by the rates of FeO_2H^- ion formation during the time the battery is on open circuit and charge, the life should be extended instead of limited, because corrosion rates are experimentally slower when the cells are standing filled with more alkaline electrolytes.

In Figure 9 it is apparent that the capacity (amp hr) would be unimpaired by the use of 1.4 sp gr of electrolyte. The averages in Table 1 show that by the use of the latter electrolyte one would reduce the hydrogen evolution rate more than one-third. Data is urgently needed to demonstrate how such a change in electrolyte concentration would affect the life of a Ni-Fe storage battery.

SUMMARY

Earlier work (2) has shown that the processes of hydrogen evolution in the first hour after a charge, were much more rapid than later and might be due in part to dissolved

hydrogen. To increase the accuracy of rate data in the first hour after charge, means were devised for computing hydrogen rates back to the hydrogen emission from the negative plate rather than merely to the rate leaving the cell as a whole. This purpose was achieved by making a hydrogen balance. The input to the head space in a cell less the output from it equals the increase in that space.

The total hydrogen evolution (Figure 1, curve No. 2), occurs according to processes expressible by three simultaneous rates: (a) the rate due to the potential of the negative plate above the stationary potential—a rapidly declining rate which becomes nearly constant within 15 minutes (Figure 1, curve No. 1); (b) the rate of desorption of hydrogen from active iron of the negative plate (Figure 1, curve No. 4), which rate is nearly zero in an hour; (c) the long-time empirical rate, the integrated form of which was developed earlier (2),

$$\text{Total Volume } H_2 = B\,t^n + C. \tag{1}$$

The above equation holds true for hydrogen from a complete Ni-Fe storage battery; that is, in the presence of generated oxygen. Through the use of data for charged negative plates promptly isolated from positive ones after charge (15), it is now found that hydrogen generated by such negatives is evolved after the first hour directly in proportion to the area of oxide-free iron in the negative plate at any time:

$$\frac{d(H_2\,\text{Volume})}{dt} = K_1(1-A). \tag{2}$$

This relation holds from about one to 1800 hours (Figure 5). When the cell stands idle the iron of the negative plate is converted to a corrosion product which is assumed to form a constant number of hemispheres around nuclei upon the metal surface.

Using a 2 N NaOH as electrolyte, Kabanov and Leikis (7) have shown that the anode process for iron occurs at 0.13 volt relative to hydrogen in the same solution and the cathode process at -0.05 volt. Their conclusions that the first process represents the solution of iron as FeO_2H^- ions have been confirmed. The cathode process, however, does not represent an equilibrium of the FeO_2H^- ion with iron hydroxide as they had inferred, but with magnetite. Furthermore, the FeO_2H^- ion was present at 10^{-7} mols per liter in both processes which they measured.

Measurements of hydrogen evolution upon stand were made using KOH up to 1.48 sp gr (15 g LiOH per liter was included). It is established that from 1.2 to 1.48 sp gr the rate of hydrogen evolution from one to 13 hours is directly proportional to the square root of the activity of water in the electrolyte. Approximately a sixfold range of water activity is represented in the data.

Evidence has been presented for the validity of

$$Fe + 2H_2O = FeO_2H^- + H_2 + H^+. \tag{5}$$

At constant hydrogen pressure the Nernst equation for Equation (5) is

$$(E_{hss})_2 - (E_{hss})_1 = \Delta E = \frac{RT}{2F} \ln \frac{(a_{H_2O})_2}{(a_{H_2O})_1}. \tag{12}$$

Equation (12) makes possible the calculation of the stationary potential of the negative plate as a function of water activity and, thus, of electrolyte concentration. The experimental changes in the stationary potential are shown in Figures 2 and 8, and in Table 1. The agreement of theory with fact is considered good. This is further evidence for Equation (5).

[redacted]

The experimental relation: Hydrogen evolution on stand is proportional to the square root of water activity in the electrolyte.

Battery capacity was found to be at a maximum with 1.3 sp gr of electrolyte which is 15 percent higher than the capacity at 1.2 sp gr. These results are in agreement with results on nickel-cadmium alkaline batteries (23). Capacities at 1.2 and 1.4 sp gr are essentially equal while the corresponding hydrogen evolutions from 1 to 13 hours are 11.8 and 6.6 liters per 1000 ampere-hours of rated capacity.

The temperature coefficient of hydrogen evolution during stand is a factor which can be used in studying the reaction mechanism in control of rate. It has been suggested that this coefficient, often expressed as an energy of activation, is consistent with a diffusion process (2,8). The activation energy for the diffusion of water is similar to that of heavy water into water, which is 4.6 to 5.3 kg cal (Table 6). The diffusion of hydrogen through iron displays energies of activation from 2.9 to 9.9 kg cal according to the allotropic form of the metal (Table 7). Energies of activation for hydrogen evolution as given in Table 4 are 5.7 to 6.0 kg cal. Judged by this factor alone, the rate-controlling process could be the diffusion of either water or of hydrogen in iron.

The mechanism of hydrogen evolution upon stand can be considered now to be well defined and due to understandable causes. There are negative iron ions formed at the same time as hydrogen gas; these ions can migrate to the positive plate, thus shortening cell life. However, since hydrogen evolution and iron ion formation are proportional and are less at electrolyte concentrations above normal, there is reason to think that higher concentration might increase cell life, rather than decrease it, and at the same time reduce the rate of hydrogen formation for batteries standing charged and idle.

* * *

REFERENCES

(1) Thomas A. Edison, Inc., Progress Report, Contract No. NObs 46607(1722), pp. 1 and 23, August 6, 1949, RESTRICTED

(2) Pitman, A. L., "Alkaline storage batteries. A critical evaluation of their characteristics," NRL Report 3618, Jan. 31, 1950, RESTRICTED

(3) Knobel, M., and Norton, R.B., "The penetration of electrolytic hydrogen through iron." J. Math. Phys. (M.I.T.) 5, 75-83 (1926)

(4) Mellor, J.W., quoting G. Neumann and F. Streintz (1892) in Modern Inorganic Chemistry, p. 125, Longmans, Green & Co., New York (1925)

(5) Platonova, I., and Levina, S., "Liberation of hydrogen on an iron cathode in alkaline solutions." J. Phys. Chem. (U.S.S.R.) 21, 331 ff. (1947)

(6) Crennell, J.T., and Lea, F.M., Alkaline Accumulators, p. 102. Longmans, Green & Co., New York (1928)

(7) Kabanov, B., and Leikis, D., "The active iron electrode in alkaline solutions." Acta Physicochimica (U.S.S.R.) 21, 769-784 (1946)

(8) Pitman, A. L., NRL ltr. rpt. C-3260-88/48, Oct. 11, 1948, RESTRICTED

(9) Darken, L.S., and Smith, R.P., "Behavior of hydrogen in steel during and after immersion in acid." Corrosion 5, 1-16 (1949)

(10) Gurney, H.P., and Lurie, J., "Charts for estimating temperature distributions in heating or cooling solid shapes." Ind. Eng. Chem. 15, 1170 (1923)

(11) Kalmykova, E., and Levina, S., "The behavior of iron electrode in alkaline solutions at low temperatures." J. Phys. Chem. (U.S.S.R.) 21, 325-330 (1947); Richards, T.W., and Behr, G.E., Z. Physik. Chem. 58, 301 (1907)

(12) Kabanov, B., Burstein, R., and Frumkin, A.,"Electrode processes." Discussions of the Faraday Society, No. 1, 259-269 (1947)

(13) Evans, U.R., "The laws of expanding circles and spheres in relation to the lateral growth of surface films and the grain-size of metals." Trans. Faraday Soc. 41, 365 (1945)

(14) Lander, J.J., (NRL) private communication

(15) Thomas A. Edison, Inc., Progress Report, Contract No. NObs 46607(1722), Nov. 6, 1948, RESTRICTED

(16) Schikorr, G., "The iron-water system." Zeit. für Elektrochem. 35, 62-65 (1929)

(17) Wagner, C., and Traud, W., "The interpretation of corrosion phenomena by superimposition of electrochemical partial reactions and the formation of potentials of mixed electrodes." Zeit. für Elektrochem. 44, 391 (1938)

(18) Pourbaix, M., "Corrosion, passivity, and passivation from the thermodynamic point of view." Corrosion 5, 121-133 (1949)

(19) Randall, Merle, and Frandsen, Mikkel, "Determination of the free energy of ferrous hydroxide from measurements of electromotive force." J. Am. Chem. Soc. 54, 40-46 (1932)

(20) Schrager, B., "Polarographic studies with the dropping mercuric cathode. I. The amphoteric nature of ferrous hydroxide." Chem. News 138, 354-356 (1929)

(21) Akerlof, G.C., and Bender, Paul, "Thermodynamics of aqueous solutions of potassium hydroxide." J. Am. Chem. Soc. 70, 2366 (1948)

(22) Latimer, W.M., The oxidation states of the elements and their potentials in aqueous solutions. Prentice-Hall, Inc., New York (1938)

(23) Schmidt, E., and Piening, W., "The behavior of alkali batteries at low temperatures." Elektrotech. Z. 14, 877-881 (1934)

(24) Glasstone, Samuel, Introduction to Electrochemistry, p. 467. D. Van Nostrand Co., Inc., New York, (1942)

(25) Orr, W.J.C., and Butler, J.A.V., "The rate of diffusion of deuterium hydroxide in water." J. Chem. Soc., 1273-1277 (1935)

(26) Temkin, M., "Diffusion of heavy water into ordinary water." Nature 136, 552 (1935)

(27) Geller, W., and Sun, Tak-Ho, Archiv für Eisenhuttenwesen 21, 423-430 (1950)

(28) Edwards, C.A., "Pickling or the action of acid solutions on mild steel and the diffusion of hydrogen through the metal." J. Iron and Steel Institute 60, 9 (1924)

(29) Barrer, R.M., Diffusion in and through solids, pp. 220-221. The Macmillan Co., New York (1941)

(30) Euringer, G., "The time effect of gas emission from heated wires in vacuo." Z. Physik 96, 37 (1935)

(31) Nelson, E.E., (NRL) private communication

(32) Bockris, J.O'M. Unpublished work mentioned in Chem. Rev. 43, 542 (1948)

(33) Thomas A. Edison, Inc., Progress Report, Contract No. NObs 46607(1722) p. 46, Nov. 6,.1949, RESTRICTED

* * *

APPENDIX
Integration of Hydrogen Rate with Time

The differential Equation (2) which was postulated, and then found to hold, for hydrogen evolved from an isolated iron plate after a charge is

$$\frac{d(H_2 \text{ Volume})}{dt} = K_1 (1 - A) \tag{2}$$

where the initial area under attack at the end of a charge is one unit of area, A represents the area covered by corrosion products at any time, t, after charge, and K_1 is the constant.

Let N equal the constant number of nuclei upon which the corrosion product forms. Assume that this product is formed into growing hemispheres with radius R at time t. Volume H_2 will represent the total hydrogen to time t. Then

$$\text{Volume } H_2 = K_2 \left(\frac{2}{3}\pi R^3\right), \tag{16}$$

$$d(\text{Volume } H_2) = K_2\, 2\pi R^2\, dR, \tag{17}$$

and

$$A = K_3 \pi R^2. \tag{18}$$

Put Equation (2) into terms of R:

$$\frac{K_2\, 2\pi R^2\, dR}{dt} = K_1 (1 - K_3 \pi R^2) \tag{19}$$

or

$$\frac{K_2\, 2\pi R^2\, dR}{(1 - K_3 \pi R^2)} = K_1\, dt. \tag{20}$$

Let a = 1, and b = $-K_3\pi$; then

$$\frac{R^2\, dR}{a + bR^2} = K_4 dt. \tag{21}$$

The left-hand side of Equation (21) integrates according to B. O. Pierce's Table of Integrals, Formulas 56 and 49:

$$\int \frac{R^2\, dR}{a + bR^2} = \frac{R}{b} - \frac{a}{b}\left[\frac{1}{\sqrt{ab}} \tan^{-1} \left(R\sqrt{\frac{b}{a}}\right)\right]. \tag{22}$$

Substitution can now be made for

$$K_5\, V^{\frac{1}{3}} = R \tag{23}$$

where V = Volume H_2 for time t.

Therefore

$$K_5 \frac{V^{\frac{1}{3}}}{b} - \frac{a}{b}\left[\frac{1}{\sqrt{ab}} \tan^{-1} K_5 V^{\frac{1}{3}} \sqrt{\frac{b}{a}}\right)\Bigg] = K_4 t + \text{constant}. \tag{24}$$

Equation (21) can be integrated into Pierce's Equation 50, a logarithmic form, if $a > 0$, $b < 0$, and these conditions are met.

$$\int \frac{R^2\, dR}{a + bR^2} = \frac{1}{2\sqrt{-ab}} \ln \frac{\sqrt{a} + R\ \sqrt{-b}}{\sqrt{a} - R\ \sqrt{-b}} \tag{25}$$

Substitute $K_5 V^{\frac{1}{3}} = R$

$$\frac{1}{2\sqrt{-ab}} \ln \frac{\sqrt{a} + K_5 V^{\frac{1}{3}} \sqrt{-b}}{\sqrt{a} - K_5 V^{\frac{1}{3}} \sqrt{-b}} = K_4 t + \text{constant}. \tag{26}$$

Since $a = 1$ and $b = -K_3 \pi$, Equation (26) becomes

$$\frac{1}{2\sqrt{K_3 \pi}} \ln \frac{1 + K_5\ \sqrt{K_3 \pi}\ V^{\frac{1}{3}}}{1 - K_5\ \sqrt{K_3 \pi}\ V^{\frac{1}{3}}} = K_4 t + \text{constant}. \tag{27}$$

The four unknown constants in Equation (27) can be determined if the values of V are known at four different times thereby establishing an equation for volume of hydrogen in terms of time of stand.

* * *

NAVY-DPPO PRNC. WASH., D.C.