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TECHNICAL NOTE 3164

FURTHER STUDIES OF THE MECHANISM BY WHICH HYDROGEN  
ENTERS METALS DURING CHEMICAL AND  
ELECTROCHEMICAL PROCESSING

By L. D. McGraw, W. E. Ditmars, C. A. Snavely,  
and C. L. Faust

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SUMMARY

The entry of hydrogen into metals from chemical and electrochemical action occurs when hydrogen-metal alloy formation is simultaneous with discharge (or release) of hydrogen atoms. This is the mechanism proposed in the earlier work by the writers (NACA TN 2696) and further supported by the current work.

The entry of hydrogen into a metal does not involve two steps whereby hydrogen first leaves its environment just outside the metal to become adsorbed on the outside and then moves into the metal adventitiously at a suitable lattice site. Conversely, neither does exit involve two steps. Hydrogen in solution in metals is characteristic of a "metal in a metal" and not of a "gas on a metal." Solubility and diffusion effects substantiate this statement, since solubility isotherms are characteristic of solutions, and not adsorption.

The conditions at a steel surface that promote even the momentary presence of hydrogen-metal alloy allow hydrogen to permeate into the steel by diffusion. Entered hydrogen does not permeate steel rapidly by a diffusion process if the hydrogen-metal alloy releases its hydrogen to the outside surroundings at a high rate, because then the concentration gradient is too low.

The hydrogen overvoltage on iron in the presence of arsenic is actually the potential of the arsine ( $\text{AsH}_3$ ) electrode. If pure iron is contaminated with arsenic on one side only, the arsine-electrode potential is transmitted through the iron to the uncontaminated side, and hydrogen permeation occurs at a high rate.

This evidence supports the concept that promoter elements in steel, such as arsenic, phosphorus, sulfur, and others, are effective in increasing the hydrogen permeability of steel by changing the overpotential relationships at the steel surface and by forming metal-hydrogen alloys of increased stability.

The variation of hydrogen overvoltage on copper cathodes with current density was shown to agree with the variation predicted by the Tafel theory of hydrogen overvoltage when the experimental order of the decomposition reaction of copper hydride is known. This supports the proposed hydrogen-entry mechanism in the case of copper, which is quite significant, because copper is an unusually poor solvent for cathodic hydrogen. For that reason, copper might be considered by some to be an exception to the entry mechanism.

Iron cathodes through which hydrogen was passed at a relatively high rate were depolarized rapidly in alkaline solution. Identical iron cathodes having the same initial potential but through which very little hydrogen was passed depolarized slowly. These results are explained by the concept that hydrogen passing through a metal can do permanent damage which makes hydrogen escape more rapidly thereafter. Thus, hydrogen passed through metal can have an effect on both the electrochemical and the physical properties of the metal.

Factors which are effective in the control of hydrogen embrittlement can be inferred from the preceding conclusions. Hydrogen entry into metals is reduced when ambient, or artificially established, conditions at the surface prevent the formation of stable hydrogen alloys or cause the rapid decomposition of any that tend to form when atomic hydrogen is available.

## INTRODUCTION

This investigation was a continuation of the efforts of the writers to develop fundamental concepts which would be useful in preventing or alleviating hydrogen damage to steel. The importance of this subject is well recognized, especially in the aircraft industry. Reference 1 presented views on the hydrogen-entry mechanism which are somewhat different from those proposed in the previous literature. Still, they are compatible with all available experimental evidence. In the present work, the phenomena relating to hydrogen entry into steel were studied further.

Many workers have postulated that hydrogen enters metals by a mechanism involving the discharge of hydrogen ions from solution, followed by adsorption on the metal surface and, finally, entry at appropriate sites. Such a mechanism requires that the hydrogen seek a site for entry after the actual discharge. The new mechanism postulates that hydrogen discharges directly into metal surfaces through the formation of metal-hydrogen alloys. This alloy formation occurs as a part of the discharge process, if there is entry of hydrogen. If there is no alloy formation, there is no entry, and any hydrogen

released by chemical or electrochemical processes not involving alloy formation ultimately bubbles off as gaseous hydrogen.

It was postulated also that anything which prolongs the life of hydrogen in the alloyed or "metallic" state will cause an increased rate of accumulation of hydrogen in the metal. The accumulation of hydrogen is decreased by conditions which cause decomposition of the metal-hydrogen alloys or reaction of the alloys with other chemical substances.

The chemical environment and the metal composition are important factors in regulating the amount of hydrogen passing into or out of the metal during chemical and electrochemical processing. The rate of transfer of hydrogen through a metal may be dependent on the entry process or on diffusion in the metal, whichever is slower, providing exit is unencumbered.

Further experimental work was needed to test the conclusions summarized above. Hydrogen-metal alloys should be electrochemically active and possibly should be responsible for the hydrogen overvoltages measured on some metals. This has been established for arsenic by previous workers (ref. 2) and it has been proposed for iron (ref. 3). Much of the work reported herein relates to testing certain important predictions which are based on the proposed hydrogen-entry mechanism. These predictions are:

(1) It is well known that different metals release hydrogen at different rates, depending on the concentration of hydroxide ion in solutions contacting them. For these metals, the hydrogen overpotential should be dependent on the pH.

(2) The relative stability of metal-hydrogen alloys produced by the cathodic reduction of hydrogen ions at metal cathodes should be associated with hydrogen overpotential.

(3) The slope of the Tafel equation for a particular metal should be predictable from knowledge of the order of the decomposition reaction of the particular metal-hydrogen alloy (or hydride). (See appendix A.)

To test these predictions, suitable metal-hydrogen alloys had to be prepared. Techniques for such preparations are not well established, and a considerable portion of the total effort had to be expended in evaluating known techniques and developing new ones.

This investigation was conducted at the Battelle Memorial Institute under the sponsorship and with the financial assistance of the National Advisory Committee for Aeronautics.

## EXPERIMENTAL PROCEDURES

The techniques and methods were generally specific for each series of experiments and therefore are described in the appropriate sections discussing the experimental work.

### EXPERIMENTAL WORK

#### Measurement of Hydrogen Overpotential Transferred

##### Through a Metal as a Function of pH

Introduction.- The postulated mechanism for hydrogen entry into metals predicts that the hydrogen overvoltage for certain metals will depend on pH by a relationship which differs from that of a reversible hydrogen electrode. The mechanism would be supported if the pH dependence could be shown to be related to the stability of the metal-hydrogen alloys formed during the entry process. The manner in which the overvoltage depends on the pH can be studied usefully only if both overvoltage and pH can be measured accurately. There is little difficulty in measuring overvoltage with reasonable accuracy. However, there is no completely successful method for measuring the pH of a cathode film. It would be incorrect to measure the pH of the solution proper, since it is related only indirectly to the pH of the cathode film.

A search of the literature revealed a way to solve this problem. In 1950, Fischer and Heiling (ref. 3) demonstrated that the potential transferred through pure-iron beakers was the true hydrogen overpotential. By this concept, hydrogen could be discharged on one side of a piece of metal and the hydrogen overpotential measured on the opposite side. The charging solution could be of any composition desired, and the solution on the opposite side could be the same or any different solution in which overvoltage measurements were desired. The transmitted-overpotential measurements could be made then in solutions of any desired pH without polarization effects or difficulties in pH measurement.

Fischer and Heiling showed that the transmitted overpotential resulted from the hydrogen transferred through the iron. The transmitted electrode potential was related to the expression:

$$E = E_r + 0.06 \log \frac{1}{[H]} = -0.06pH - 0.06 \log [H] \quad (1)$$

In equation (1),  $[H]$  represents the concentration of hydrogen atoms in the metal surface. Except when inhibitors were used, the electrolytes were the same on both sides of the iron. A plot of their transferred hydrogen overvoltage versus the logarithm of the current density gave a slope which agreed with the classical hydrogen-overpotential mechanism proposed by Tafel.

These results show that the hydrogen-entry mechanism postulated by the writers is in accord with Tafel's theory. Each proposes that dissolved hydrogen is responsible for the respective phenomena of interest. Fischer and Heiling stated that no other factors could be responsible for the transmitted overpotential, since there was no deposition of  $H_3O^+$  ions on the surface where the measurements were made.

This transmittal of overpotential must take place by the formation of metal-hydrogen alloys. The slow decomposition of these alloys determines the overvoltage and is dependent on pH. An experiment was designed to show either (1) the pH-dependent term in equation (1) is completely responsible for any variation in a nonreversible hydrogen overpotential with pH or (2) pH can have an effect on the electrode potential not indicated by the equation. The secondary effect expected was that hydroxide ion would catalyze the release of hydrogen from iron-hydrogen alloys. This action would depolarize the electrode considerably by reducing the steady-state concentration of hydrogen in the metal.

Apparatus and procedure.- Figure 1 is a schematic drawing of the apparatus used to measure the transmitted hydrogen overvoltage. A pure-iron beaker was suspended inside a glass beaker. An inner electrolyte was placed inside the iron beaker and an outer electrolyte occupied the space between the two beakers. Platinum anodes were suspended in the outer electrolyte and the iron beaker served as a cathode.

When this circuit was electrolyzed with a direct-current source, hydrogen ion was discharged at the outer surface of the iron beaker. A saturated-calomel electrode was placed in the inner electrolyte and connected with the iron beaker through an electronic potentiometer. Thus, it was possible to measure (1) the electrode potential of the inside surface of the iron beaker before electrolysis, (2) the transmitted potential during electrolysis when hydrogen was being discharged on the outside surface, and (3) the transmitted potential immediately after electrolysis was discontinued. The effect of pH on the transmitted potential could be observed by changing the pH of the inner electrolyte.

The iron cup was machined from a massive ingot of pure iron.<sup>1</sup> It was placed on a pure-iron setter plate in a vacuum furnace (less  $1 \times 10^{-5}$  millimeter of mercury pressure), annealed at  $1,000^{\circ}$  C, and then cooled under vacuum. A liquid-nitrogen trap was used to protect the system from contaminating vapors. The purity of the setter plate was equivalent to that of the iron beaker. The annealed cup was stored in a clean desiccator until used for overvoltage experiments.

Just previous to its use, the cup was dipped in dilute hydrochloric-acid solution until gassing was observed. Then it was washed in distilled water and placed in the apparatus with inner and outer electrolytes as shown in figure 1.

Two outside electrolytes were used in the experiments: (1) 2 percent by volume of sulfuric-acid (1.84 specific gravity) solution and (2) 1 gram per liter of  $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$  in the 2-percent sulfuric-acid solution. Solution (1) represents a good hydrogen-charging solution and solution (2) is one of the most active charging solutions known. Solution (1) was preelectrolyzed using platinum anodes and cathodes for 30 minutes at a current density of 144 amperes per square foot prior to use with the iron beaker.

The inner electrolyte was a 0.1-molar sodium-sulfate solution prepared from the chemically pure salt and distilled water. The pH of this solution was adjusted by adding dilute sulfuric-acid or dilute sodium-hydroxide solutions. The value of the pH was measured with precision test papers before and after each set of potential readings. The estimated maximum uncertainty in pH was  $\pm 0.5$  unit.

Before each set of potential measurements, the cup was washed with distilled water and filled with a new portion of inner electrolyte.

The electronic potentiometer used in measuring the potential of the inner surface of the cup had an estimated accuracy of  $\pm 0.002$  volt per reading. The precision of measurement from run to run was estimated to be about  $\pm 0.010$  volt. The outer area of the immersed portion of the cup was 4.0 square inches. The charging current was always 2.1 amperes and the charging voltage, 4.2 volts.

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<sup>1</sup>Obtained from the National Research Corp., Cambridge, Mass. A typical analysis, in percentage, supplied with the ingot was:

Fe, approximately 99.95	Al, <0.001	Cu, <0.001	Si, <0.01
N, <0.001	C, <0.005	Mn, <0.001	Sn, <0.001
O, <0.02	Cr, <0.001	Mo, <0.001	Ti, <0.001
H, <0.005	Co, <0.001	Ni, <0.001	W, <0.001



A set of potential readings was taken for a given pH following 20 minutes of charging when it appeared that a relatively steady state had been reached. Each set of potential readings consisted of four to five pairs of readings, one taken with the current on and one taken 1 or 2 seconds after the current had been shut off. The time the readings were taken after the current had been shut off was recorded, as these readings represented decay of potential with time. There were never any erratic fluctuations of potential during the measurements. Similar procedures were followed with the arsenic-containing charging electrolytes. The pH values of the inner electrolyte were 2, 6, and 13 for separate sets of measurements.

Results and discussion.- For the arsenic-free charging electrolyte, the rate of change of transmitted potential versus pH was  $-0.02 \pm 0.002$  volt per pH unit, as shown in figure 2. The rate of change for the reversible hydrogen electrode (reduction of water) is  $-0.059$  volt per pH-unit increase. These values are plotted in figure 2 for comparison with the measured values.

When arsenic was added to the charging electrolyte, the transmitted potentials varied with pH change at a different rate. For this case, the slope was  $-0.007$  volt per pH unit, as shown in figure 3. The immediate depolarization noted on opening the circuit was greater when arsenic was present in the charging electrolyte.

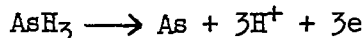
The transmitted potentials plotted in figure 3 cannot be compared accurately with those of figure 2, because arsenic in the charging electrolyte changes the overpotential for a given current density. Before arsenic was added to the charging electrolyte, no hydrogen evolution had been observed from the inside wall of the iron cup during charging, except when the pH inside the cup was low, when the iron was chemically attacked there.

When arsenic was present in the charging electrolyte, hydrogen evolved from the inside wall of the cup during all measurements. With the current off, this evolution ceased in about 5 minutes. Arsine was evolved in the cathode gas on the outside of the cup during charging. It is evident that the concentration of hydrogen at the inner surface of the cup was much greater when arsenic, a hydrogen-alloy former, was present in the charging electrolyte.

Significantly, the measured transmitted potentials are below the decomposition potential for water up to pH values over 11.0. This pH, at which hydrogen-charged iron has the same potential as a reversible hydrogen electrode, remains approximately the same, whether the iron is charged in the presence or in the absence of arsenic. The potentials are not alike at any other pH. The plot of data for the arsenic-free charging electrolyte (fig. 2) intercepts  $\text{pH} = 0$  at a potential within

0.006 volt of the overvoltage of hydrogen on iron (0.40 volt), as determined by the "interrupter" method (refs. 4 and 5) or the "direct" method (ref. 6) at a low current density (1 ampere per square foot).

With arsenic in the bath, the plot (fig. 3) intercepts  $\text{pH} = 0$  at  $-0.818$  volt. This value is between the reversible electrode potential of



as reported by Latimer (ref. 7) by estimation from thermal data ( $-0.60 - 0.246 = -0.846$ ) and that reported by Latimer and Hildebrand (ref. 8) ( $-0.54 - 0.246 = -0.786$ ). The factor  $-0.246$  is the potential of the saturated-calomel electrode and is added to the half-cell potential of the arsine electrode. Thus, the transmitted potential is actually the potential of the arsine electrode. This appears to be definite confirmation of the postulated entry mechanism as related to the formation of metal-hydrogen alloys or hydrides. The  $\text{AsH}_3$  formation was responsible both for the entry of hydrogen into pure iron and for the measured overpotential.

The different rates of change of potential with  $\text{pH}$  in figures 2 and 3 are significant. Neither plot has a slope of  $-0.06$ , as demanded of a reversible hydrogen electrode. The facts that both electrodes have the same potentials at  $\text{pH} = 11$  and that this potential is the potential of the hydrogen electrode are merely fortuitous. At  $\text{pH} = 11$ , both electrodes have the same concentrations of electrochemically active hydrogen, showing that the catalytic loss of hydrogen from iron in the presence of base has been more rapid in one test than in the other.

The relative rates of depolarization of the transmitted hydrogen overpotential are shown in figure 4 for the arsenic-free charging electrolyte and in figure 5 for the arsenic-containing electrolyte. In general, depolarization was more rapid in basic solution, no matter which charging electrolyte was used. More rapid depolarization followed charging with the arsenic-containing electrolyte.

The negative slope for the curves in figure 4 where  $\text{pH} = 2$  can be accounted for, since the acid was attacking the iron. Thus, by a chemical process, more hydrogen was entering the metal (forming a metal-hydrogen alloy) than was leaving it. This caused polarization, instead of depolarization.

The difference in relative positions of the curves for  $\text{pH} = 6$  and  $\text{pH} = 13$  in figures 4 and 5 is believed to be related to the effectiveness of the bases in catalyzing the release of hydrogen from annealed iron and from iron cold-worked by the passage of hydrogen. At any rate,

these experiments show that  $\text{OH}^-$  ions are catalytically active in decomposing the iron-hydrogen alloys formed during chemical or electrochemical processing.

Conclusions.- The following conclusions are drawn from the results of this series of tests:

- (1) Hydrogen in solution in iron is electrochemically active.
- (2) Hydrogen in solution in iron is responsible for the measured overpotential.
- (3) The release of hydrogen from solution in iron is accompanied by a drop in measured potential.
- (4) Solutions of hydrogen in pure iron must be stabilized at the entry face to obtain a high permeation rate (as by addition of arsenic to the charging solution).
- (5) The transmitted overpotential of hydrogen on iron is dependent on the pH at the surface where the potential is measured.
- (6) The transmitted overpotential of hydrogen on iron is depolarized rapidly in basic solution, possibly by catalytic release of electrochemically active hydrogen from solid solution in iron.
- (7) The low incidence of embrittlement of metals by treatment in basic solutions as opposed to acid solutions or those containing embrittlement promoters results from the instability of iron-hydrogen alloy in basic solution and the consequent low permeability to hydrogen.

Permeation is low when the surface-formed metal-hydrogen alloy is not stable enough to hold the hydrogen for subsequent diffusion through the metal. Arsenic-hydrogen alloy (arsine) forms readily enough and is stable enough to perform these functions.

#### Potentials of Chemically and Electrochemically Prepared

##### Solid Solutions of Hydrogen in Iron

Introduction.- The potential of a solid solution of hydrogen in iron is determined by the constituent which is most active electrochemically, hydrogen, and should be independent of how the solid solution was prepared. The potentials should vary with the concentration of hydrogen in solid solution, with temperature, and with the pH of the solution in which the potentials are measured.

The term "solid solution," as used herein, designates a metastable solid solution of hydrogen in iron. The equilibrium solubility of hydrogen in iron at atmospheric temperatures is very low. However, a considerably greater amount of hydrogen can be introduced into iron under nonequilibrium conditions, as by cathodic charging. A metastable alloy results. This alloy is termed a solid solution unless evidence of hydride formation is noted.

These metastable alloys of iron and hydrogen can be prepared in a variety of ways, including cathodic charging, acid pickling, and chemical reduction of iron salts.

Saturated solid solutions having identical potentials may become noble at much different rates as they lose hydrogen. It is assumed here that different rates of depolarization among a group of iron-hydrogen alloys are indicative of physical differences. Such differences may be in the form of aggregation, as for a powder versus a massive material, or in terms of cold-work, internal stress, grain size, and so forth. The amount of hydrogen transported through the metal during charging may be a factor, even though most of it has left the metal. It is well established that hydrogen passing through iron leaves it in a cold-worked condition (refs. 9, 10, and 11).

A number of experiments were performed to study the electrochemical behavior of solid solutions of hydrogen in iron as prepared by various methods.

Procedures and materials.- Codeposition of iron and hydrogen was one of the methods of preparation studied extensively. The deposits were formed on platinum cathodes under various experimental conditions from a solution containing 875 grams per liter of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ . In general, the solutions were considerably below atmospheric temperatures. Iron anodes were used. Immediately upon removal from the plating solution, each plate was rinsed in several portions of the electrolyte that was used for the subsequent potential measurements. These rinse solutions were kept at  $0^\circ\text{C}$  or lower to avoid decomposition of the metastable solid solutions.

An electronic potentiometer and a saturated-calomel electrode were employed to measure the potentials. Measurements were made within 1 minute after deposition was stopped and periodically thereafter for approximately 15 minutes. Temperatures were  $5^\circ$ ,  $15^\circ$ , and  $25^\circ\text{C}$ . The acidity of the solutions used in the potential measurements was determined with a low-temperature glass electrode.

As a check on the electrode system and the potentiometer, the potential of a pure-iron sample was measured under the same experimental conditions as used for each electrodeposited sample. The pure-iron

electrodes were cut from the ingot used to make the iron cup for the transmitted-potential work.

Chemically prepared iron-hydrogen solid solutions were obtained by the reaction of phenyl magnesium bromide and anhydrous ferric chloride in ether solution. This reaction has been reported in the literature (refs. 12 and 13) as a method of preparing iron hydride, although the present work and consideration of the published data lead to the conclusion that iron-hydrogen solid solutions are produced, instead of iron hydride.

Other methods of preparing iron-hydrogen alloys chemically were tested, but none of the products appeared worthy of further experiments.

Experiments in cathodic charging to form iron-hydrogen alloys already have been described in the section on transmitted potentials.

Results.- All the results of potential measurement on the codeposited iron-hydrogen solutions are recorded in table 1, along with data on conditions for obtaining the deposits. The potentials were -0.77 to -0.88, over the pH range from 3.3 to 10.3 for all specimens which were not degassed before measurement.

The potential of the chemically prepared iron-hydrogen solid solution, measured at 5° C in saturated potassium-chloride solution, was  $-0.83 \pm 0.05$  volt within a minute after assembly of the electrode system. The potentials of the saturated solid solutions prepared by cathodic charging of pure iron with hydrogen (fig. 2) were -0.73 to -0.87, over the pH range from 4 to 10.

Note in table 1 that a number of the potentials of hydrogen-iron solid solutions were measured in the presence of 1.0-normal ferrous sulfate and still were highly cathodic. This proves that the iron-ferrous-iron half-cell potential was not being measured and was not interfering with the results.

The potentials determined for the alloys prepared by the three different methods were very nearly alike, yet the relative rates at which the alloys became noble through loss of dissolved hydrogen varied widely. Data in table 1 and figures 4 and 5 show this clearly.

Rapid depolarization was not associated with a fine state of subdivision of the metal. The most rapidly depolarized iron was that massive iron which had been charged with, and extensively permeated by, hydrogen through cathodic pickling in acid containing arsenic (fig. 5). Within seconds, this metal became more noble than iron charged with hydrogen in pure acid (fig. 4).

Discussion and concluding remarks.- These results are highly significant. They show that, no matter how the solid solutions of hydrogen in iron were prepared, they all exhibited the same electrochemical potential, thus indicating that the solid solution was saturated. The results also show that solid solutions, rather than hydrides, were formed, because the electrochemical potential of the materials changed in a regular fashion as hydrogen was lost. For a hydride, the potentials would remain constant as long as any significant amount of hydride remained.

The formation of iron-hydrogen solid solutions or alloys by electrolytic charging or codeposition is directly analogous to situations occurring in industrial fabrication operations. However, promoter elements, such as arsenic, phosphorus, and sulfur, are always present in steel, and so hydrogen entry is facilitated. Even minor amounts of the promoter elements can have very significant effects.

#### Potential of Chemically Prepared Copper

##### Hydride as a Function of pH

Introduction.- Studies with copper hydride offer a means for further checking the preceding experimental data and conclusions. Copper hydride lends itself to study in aqueous systems because it is metastable and yet does not decompose too rapidly. Also, copper commonly is involved in electrochemical processing operations. The potential of copper hydride should vary with the pH of the solution in which the potential is measured in the same way that the potential of a reversible hydrogen electrode varies with pH. It is assumed that the electrochemically active hydrogen in the hydride is in a standard reference state (activity of 1). This distinguishes the electrochemical behavior of hydrides from the behavior of solid solutions, as discussed in the preceding section.

The catalytic decomposition of copper hydride would not be expected to change the electrochemical activity of hydrogen in the hydride so long as a significant amount of hydride remains present. Consequently, the difference between the potential of the hydride in solutions of different pH values and the potential of a reversible hydrogen electrode in solutions of the same pH values should be constant. This constant difference is proposed to be the overpotential of hydrogen on copper. It is expected to be independent of pH.

Experimentally, the overvoltage can be claimed constant if the measured rate of change of the potential of copper hydride with pH is -0.06 volt per pH unit, according to equation (1). The following experiments were made to determine the pH coefficient of copper-hydride potential in aqueous solutions.

Materials and procedure.- Copper hydride was prepared by the method given by Feitknecht and Warf (ref. 14). The following solutions were prepared and mixed together:

(1) 66 grams of chemically pure  $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$  in 50 milliliters of  $\text{H}_2\text{O}$  (at  $50^\circ \text{C}$ )

(2) 50 grams of chemically pure  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in 100 milliliters of  $\text{H}_2\text{O}$  (at  $50^\circ \text{C}$ )

(3) 20 milliliters of chemically pure  $\text{H}_2\text{SO}_4$  (specific gravity 1.84) in 180 milliliters of  $\text{H}_2\text{O}$  (at  $50^\circ \text{C}$ )

The mixture was allowed to react for 15 minutes with constant stirring. The temperature was maintained at  $50^\circ \text{C}$ . The reaction was then stopped by dilution with cold distilled water.

The copper hydride produced by the reaction was washed at least seven times with distilled water by decantation. Then it was stored under distilled water until used. After about 2 days of storage at  $22^\circ$  to  $30^\circ \text{C}$ , most of the hydrogen had escaped.

Potential measurements were made on the copper hydride within 1 day of the preparation. Portions of the material were washed several times with portions of the electrolyte of chosen pH which was to be used for the measurements. The resulting slurry was placed in a test tube with a hole in the side wall about an inch above the slurry. A platinum electrode sealed into a glass tube was inserted in the slurry. The assembly was then immersed in a beaker containing a new portion of the electrolyte used for the washing.

A saturated-calomel electrode was used to measure the potential of the slurry. Readings were made immediately after assembly of the electrodes and thereafter at 1-minute intervals. Readings were continued for an hour in some cases. It was impossible to estimate the precision of these tests, because the readings were erratic and often fluctuated unaccountably.

The unbuffered solutions in which the potentials were measured were prepared from distilled water and chemically pure sulfuric acid. The buffered solutions were prepared from phthalic acid and its potassium salts and were approximately 0.2 normal. The pH of each solution was measured with a low-temperature glass electrode. The pH values ranged from 2 to 6.

Results.- The measured potentials are recorded in table 2. The copper hydride behaved like copper metal in all of the unbuffered solutions and in the buffered solutions up to a pH of between 2.95 and 3.3. Decomposition of the hydride was slow in these acid solutions.

The hydride decomposed vigorously in buffered solutions over the pH range from 3.3 to 5.7, and the electrode potential was much less noble than that characteristic of copper. Moreover, the pH coefficient of the initial potential readings in these solutions was -0.06, within the limits of experimental error. The potentials measured 15 minutes to 1 hour after assembly of the electrodes were much more noble. The platinum electrode became coated with spongy copper during this time interval.

A decrease in potential with time, approaching the potential of copper metal in the same solution, was always observed. This depolarization was present, but very gradual, during the first minute after the electrodes were assembled in buffered solutions. Only after approximately 1 minute did the potentials fluctuate greatly, while changing toward the potential of copper metal. Agitation of the platinum electrode during the measurements resulted in potentials which were less negative than those recorded in table 2. The recorded potentials are for quiescent electrodes.

Discussion and concluding remarks.- The potential of copper hydride varied with pH in the same way as the potential of a reversible hydrogen electrode over a fairly broad range of pH values. This indicates that a true hydride was prepared. The hydride was electrochemically active for only short periods of time because it decomposed. Thereafter, copper covered the undecomposed hydride and resulted in more noble potentials. Much more significant potential measurements of copper hydride might have been obtained if the hydride electrode had been a mixture of powders of copper hydride and an inert conductor (carbon). This thought arose too late in the experimental program to be checked.

Apparently, the hydrogen in copper hydride is not electrochemically active at low pH values in buffered solutions or at any pH in unbuffered solutions. In these situations, the more noble potential of copper metal is observed. At higher pH values in buffered solutions, a general base catalysis is responsible for promoting decomposition of the hydride and rendering the hydrogen in it electrochemically active. This means that the reaction  $H[\text{in Cu}] \rightarrow \text{Cu} + H^+ + e$  can proceed with sufficient speed to become responsible for a measurable potential without polarization.

In the higher range of pH values the pH coefficient of -0.06 indicates that the activity of hydrogen in a hydride determines the potential. However, a change in potential with time was observed, indicating solid-solution behavior. Actually, copper resulting from decomposition of the hydride particles probably covered the undecomposed hydride, causing the change to more noble potentials. The proof that this hydrogen-copper alloy is a true hydride indirectly supports the



proposed mechanism for entry of hydrogen into metals by explaining the hydrogen overvoltage on copper properly.

Copper has been considered an exception to the Tafel mechanism by some investigators. Appendix A describes how the kinetic order of the decomposition reaction for copper hydride prepared by the method given herein gives a correct value for the slope of the Tafel lines. Thus, hydride formation in the case of copper can explain both hydrogen entry into copper and the hydrogen overvoltage on copper.

These results show that copper is not an anomaly among the metals, and its performance can be explained by the new hydrogen-entry mechanism.

#### Correlation of Hydrogen Content of Steel With Relative Degree of Embrittlement

In reference 1, it was shown that certain coatings (notably potassium chloride, arsenic, and lead) inhibit the exit of hydrogen from metals. SAE 4130 steels which were coated with these materials on one side and cathodically treated with hydrogen on the other side exhibited permeabilities to hydrogen and degrees of embrittlement which were different from those of the same metal which was not coated. This phenomenon led to the hypothesis that the embrittling effect was related to the amount of hydrogen which had passed through the metal but was no longer present.

Several investigators (refs. 9, 10, and 11) have shown that iron is cold-worked by the passing of hydrogen through it. However, there is no previous evidence that prevention of the exit of hydrogen should have any effect on the amount of hydrogen taken up by iron or on the degree of embrittlement. There is a possibility that more damage is done to iron when a relatively large amount of hydrogen is passed through it than when the exit is blocked so that a back pressure builds up to limit diffusion from the entry side.

In the present program, the previously reported results could not be reproduced, and no new data of interest in this matter were obtained. The experiments are described in appendix B. Tests were made with steel specimens which proved unsuitable for this work. It is now possible to outline the proper steps for further efforts to study the effect of hydrogen passed through steel versus hydrogen retained in steel.

Larger steel specimens should be used for greater accuracy of hydrogen analyses. Also, the steel should be preferably less susceptible to embrittlement than SAE 4130. This steel was used because of its interest to the airframe industry. However, it is now evident that experimental

results on the effect of hydrogen in steel can be obtained more readily with a steel which is less susceptible to hydrogen. The results of these tests could be interpreted then as they relate to SAE 4130 or other more susceptible steels.

Battelle Memorial Institute,  
Columbus 1, Ohio, March 15, 1953.

## APPENDIX A

EVIDENCE TAKEN FROM RECENTLY PUBLISHED LITERATURE WHICH SUPPORTS  
THE PROPOSED HYDROGEN-ENTRY MECHANISM

It has been assumed generally that, for the Tafel mechanism to apply to hydrogen overpotential, the slow process of recombination of hydrogen atoms must be a second-order reaction. This can be seen as follows:

Let  $n = [H]$  = Concentration of H atoms per square centimeter across which passes a current density  $i$ ; then, neglecting anodic current,

$$E - E_r = \eta = \frac{RT}{F} \log_e \frac{1}{n}$$

where

$E$  measured potential

$E_r$  potential on reversible hydrogen electrode

$\eta$  hydrogen overpotential

$R = 1.987$  calorie per mole-degree

$T$  absolute temperature

$F = 23,070$  calories per volt-gram-equivalent

But  $n = \sqrt{ki}$  if the reaction  $MH + MH \rightarrow H_2$  (gas) is of the second order; hence,

$$\eta = A - \frac{RT}{2F} \log_e i$$

where  $A$  is a constant at constant  $T$ .

The present mechanism for hydrogen entry views the process of recombination as the decomposition reaction of metal hydrides (and/or solid solutions). This decomposition process does not have to be second order; hence, for the Tafel mechanism to apply, the slope of the line of

$\eta$  versus  $\log_e i$  does not have to have the constant value  $\frac{RT}{2F} \times 2.303$  but will vary according to the kinetic order of the decomposition reaction.

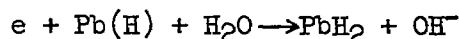
Feitknecht and Warf (ref. 14) showed that the order for the decomposition reaction of copper hydride was nearly unity. At 25° C, this will give a value of the slope for the Tafel equation of

$$\frac{RT}{F} = b = \frac{1.987 \times 298.1 \times 2.303}{1 \times 23070} = 0.059$$

A recent paper by Hiskey and Senett (ref. 15) gives values of  $b$ , the slope of the Tafel line, equal to 0.056, 0.059, and 0.067.

Considering the large experimental errors involved in both kinetic and overpotential measurements, the  $b$  values of Hiskey and Senett are in excellent agreement with the value demanded by the present hydrogen-entry mechanism.

It has been claimed (ref. 16) that lead cathodes disintegrate into colloidal lead at high current densities by quantitative formation and subsequent decomposition of a volatile unstable hydride of lead. The equation for the formation of  $PbH_2$  is considered to be:



which is a paraphrase of the mechanism for hydrogen entry into metals proposed herein.

Some investigators are of the opinion that the Tafel equation receives more attention than it deserves and that various "diffusion layers," "double layers," and "energy barriers" for ion transfer and for ion discharge deserve major emphasis in future work. However, it is the opinion of the present authors that the physical picture of the Tafel mechanism is descriptive and reduces the complexity of polarization during hydrogen deposition. Since Fischer and Heiling (ref. 3) have shown that true hydrogen overvoltage can be transmitted through metal to a site where other forms of polarization are absent, the simple Tafel mechanism should be retained.

## APPENDIX B

EXPERIMENTS ON EFFECT OF HYDROGEN CONTENT ON  
BEND ANGLE FOR STEEL SPECIMENS

The objective of this particular experimental work was to observe whether inhibiting the exit of hydrogen from a metal being cathodically charged would cause a change in the permeability of the metal to hydrogen and change the amount of embrittlement incurred by the metal. Any observed changes in permeability and embrittlement were to be correlated either with differences in hydrogen contents of the steel or with differences in the quantities of hydrogen which had passed through the metals.

It was hypothesized that, if a difference were observed in embrittlement due to the hydrogen that had passed through the metal, and if dry potassium chloride, arsenic plate, or lead plate prevented loss of hydrogen from the exit face, then the sample with dry potassium chloride, arsenic plate, or lead plate should have a different residual hydrogen content from that of a similar sample without these coatings for identical charging conditions. The coated metal would not necessarily have a higher hydrogen content after charging. Its permeability and capacity for hydrogen might not be so great as those of the metal through which more hydrogen had passed. In addition, since aluminum citrate inhibited embrittlement when present in the charging electrolyte, it was reasoned that considerably less hydrogen must have diffused into the metal. The following experiments were designed to test these hypotheses by correlating the hydrogen content plus the amount passed through hydrogen-embrittled steel with the relative degree of embrittlement.

## Materials and Experimental Procedure

Specimens to be used for cathodic charging and hydrogen analysis were cut from a plate of SAE 4130 steel in a uniform direction by a shearing press and then machine finished. The final dimensions were 1/4-inch width, 3-inch length, and 3/32-inch thickness.

The specimens were given a complete anneal by packing in iron chips and heating to 1,550° F for 1 hour, and furnace cooling. After the anneal, the specimens were heat-treated as follows:

- (1) Preheated at 800° F for approximately 1 hour
- (2) Heated to 1,575° F for 20 to 25 minutes in a controlled-atmosphere furnace and then quenched in oil

- (3) Tempered at 1,000° F for 2 hours to 36 to 37 Rockwell C
- (4) Retempered at 1,025° F for 2 hours to 34 to 35 Rockwell C

The specimens were cleaned and prepared as follows:

- (1) Solvent degreased
- (2) Scale removed with coarse belt sander
- (3) Scribed and punched for identification
- (4) Solvent degreased
- (5) Desiccated until used for cathodic charging; followed by hydrogen analysis

The specimens were coated on one side with Pyseal (a low-melting-point wax), or with dry potassium chloride plus Pyseal, before being charged cathodically with hydrogen. After cathodic charging, all the Pyseal was removed before the sample was stored under mercury for hydrogen analysis by the tin-fusion method (ref. 17). After each specimen had been charged with hydrogen, it was cleaned, dried, and cut into 1-inch pieces with a bolt cutter. Those sections which had been charged cathodically were stored under mercury within  $2\frac{1}{2}$  minutes after cathodic charging in one of the following baths:

Bath A: 10 percent by volume sulfuric acid prepared from chemically pure reagent-grade sulfuric acid (specific gravity 1.84)

Bath B: Bath A saturated with chemically pure carbon tetrachloride

Bath C: 150 grams of chemically pure citric acid monohydrate plus 150 grams of aluminum sulfate (as chemically pure dry powder) plus 1,350 milliliters of water

In every case, a bright platinum anode was used in the electrocharging bath. Each specimen was exposed to the charging electrolyte under conditions described in table 3 (experiments 40 to 49).

The SAE 4130 steel specimens used for embrittlement tests (experiments 50 to 74) differed in thickness and hardness from those used for hydrogen analysis in experiments 40 to 49. The thicker specimens allowed greater accuracy in hydrogen analysis and the thinner and harder specimens were more suitable for ductility tests. They were machined from  $3/32$  inch to  $1/16$  inch and then were given the following heat treatment:

- (1) Preheated for 1 hour at 800° F
- (2) Heated at 1,550° F for 20 minutes and then quenched individually in oil
- (3) Tempered 1 hour at 715° F and cooled
- (4) Tempered 3/4 hour at 750° F and cooled
- (5) Tempered 1 hour at 800° F

The specimens with this treatment were in group A. The samples in group B were tempered for an additional hour at 850° F. Two Rockwell hardness measurements were made on each sample.

The specimens were sealed into a Lucite cell (shown in fig. 6) with high-purity paraffin wax just before cathodic charging with hydrogen.

The question of whether the wax affected the hydrogen entry might be raised. The results of the work, however, indicate that the presence of wax was not related to any difficulty in achieving reproducibility of results.

Using the cell constituted a variation of the method of using Pyseal to prevent electrolyte contact with certain parts of the cathode. With this cell, it was easy to observe whether the dry potassium chloride (when used) on the back of the cathode became wetted during the run.

The dry potassium chloride was prepared as a very fine suspension of the salt by pouring a small volume of its saturated aqueous solution into a large volume of chemically pure acetone. One side of the specimen was covered with the suspension and then the sample was allowed to dry thoroughly. High-purity dry nitrogen was blown into the dry side of the cell to keep moisture out during cathodic charging of the samples.

Bath A used for electrolysis was 10 percent sulfuric acid by volume. During the 4-minute interval between the time when each sample was removed from the charging bath and the time when it was bent, the sample, in each experiment, was rinsed in tap water and air-dried.

#### Results and Concluding Remarks

Residual hydrogen contents are given in table 3 for specimens of SAE 4130 steels which were charged electrolytically with hydrogen under the conditions described therein. The results of ductility tests are recorded in table 4. There is no indication that dry potassium chloride had an effect on the degree of embrittlement incurred during charging, as was shown in the earlier work.

The poor reproducibility of these results did not allow any interpretation of the experiments. The scatter observed in ductility values probably is related to the greater hardness of the specimens compared with the hardness of the specimens used in the previous work. The harder specimens were so susceptible to embrittlement that their ductilities varied widely after any type of cathodic treatment, or even before treatment.

Chaudron (refs. 9 and 10) showed that cold-working is produced in pure iron by cathodic hydrogen that has entered into and then emerged from the iron. Large quantities of hydrogen must enter and emerge over a considerable period of time before permanent cold-working damage is achieved. This is consistent with the fact that repeated cathodic charging of a steel specimen increases its permeability and occlusive capacity for hydrogen. It is also consistent with the fact that mechanical cold-working increases both the permeability and the occlusive capacity of steel for hydrogen. Checking for this effect was the objective of the present experiments with steel. If such an effect had been found, the mechanism under study on this project would have been supported. Exit of hydrogen by release from solid solution would have been prevented by materials known to stabilize hydrogen-iron alloys. It would be of practical value to know the minimum amount of hydrogen required to cause permanent damage by passing through steel.

Experiment 74 (table 4) in the present research showed that no hydrogen evolved from the exit face of the steel in the 10-minute period of charging, even when a hydrogen-entry promoter was present in the charging electrolyte and blisters were formed, showing that large quantities of hydrogen had entered.

It is possible that potassium chloride does not exhibit the same behavior as arsenic and lead with regard to inhibiting the release of hydrogen from metals, such as was indicated by the work of the previous project. New work should involve the use of arsenic plate or lead plate, instead of potassium chloride.



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TABLE 1.- ELECTRODE POTENTIALS OF CODEPOSITED IRON-HYDROGEN PLATES

Experiment	Material measured and preparation	Temperature at which potential was measured, °C	pH	Electrolyte	Time of measurement, min		Remarks
					(a)	(b)	
6	Pure-iron sample, surface cleaned with chemically pure solvents and then dried	5	5.4	Saturated KCl	-0.360	0, 1, 3	Solution stirred continually. Readings steady.
7	Annealed bright platinum	5	5.4	Saturated KCl	.237	0, 1, 3	Solution stirred. Readings steady.
8	Annealed bright platinum, one side covered with platers' masking tape	5	5.4	Saturated KCl	.220	0, 1	Solution stirred. Readings steady.
9	Codeposited hydrogen-iron plate Temperature of deposition bath, -25° C Total current, 1.5 amp (raised slowly from 0 amp) Bright-platinum-cathode area (one side covered with platers' masking tape), 2 sq in. Plating time, 5 min	5	5.4	Saturated KCl	-.859	0, 1, 3	Solution stirred. Readings were steady and did not drift. Plate was black and flaky in appearance and released hydrogen at a steady rate throughout measurements. Placing plate in distilled H <sub>2</sub> O at 25° C after measurements caused an immediate increase in decomposition rate.
10	Codeposited hydrogen-iron plate prepared as in experiment 9	5	5.4	Saturated KCl	-.840	0, 1, 3	Same as for experiment 9.
11	Pure-iron sample, cleaned surface	15	5.3	Saturated KCl	-.361	0, 1, 3	Solution stirred. Readings steady.
12	Codeposited hydrogen-iron plate prepared as in experiment 9	15	5.3	Saturated KCl	-.827	0, 1, 3	Solution stirred. Readings steady. Plate was releasing hydrogen vigorously during readings.
13	Codeposited hydrogen-iron plate prepared as in experiment 9	15	5.3	Saturated KCl	-.827	0, 1, 3	Same as for experiment 12.

<sup>a</sup>All potentials are recorded with reference to saturated-calomel electrode as zero at temperature of measurement.  
<sup>b</sup>The operation of rinsing specimens and transferring them to potential-measuring apparatus took less than a minute. Therefore, zero (0) time for potential measurements was no more than 1 minute after removal of specimens from plating bath.

TABLE 1.- ELECTRODE POTENTIALS OF CODEPOSITED IRON-HYDROGEN PLATES - Continued

Experiment	Material measured and preparation	Temperature at which potential was measured, °C	pH	Electrolyte	Potential, v	Time of measurement, min	Remarks
					(a)	(b)	
14	Codeposited hydrogen-iron plate Temperature of deposition bath, 25° C Total current, 1.5 amp Plating time, 5 min Platinum-cathode area, 2 sq in., one side covered with platers' masking tape	5	5.4	Saturated KCl	-0.778	0, 1	Solution stirred. Readings steady. No gas released during measurements. Following measurements, plate was placed in distilled H <sub>2</sub> O. There was slight bubbling at edges where current density was highest during plating.
15	Codeposited hydrogen-iron plate Temperature of deposition bath, -25° C Total current, 2 amp (raised slowly from 0 amp) Plating time, 5 min Platinum-cathode area, 4 sq in. Resulting plate was washed, dried, and stored under anhydrous ether for 3 hr to degas. At end of this time, plate released no more hydrogen.	5	4.4	Saturated KCl	-.648	0, 1	Solution stirred. Readings steady.
16	Pure-iron sample, surface cleaned	5	4.4	Saturated KCl	-.448	0, 1	Solution stirred. Readings steady.
17	Bright platinum, annealed	5	4.4	Saturated KCl	.248	0, 1	Solution stirred. Readings steady.
18	Codeposited hydrogen-iron plate, deposited as in experiment 15, but not allowed to degas before potential measurements	5	4.4	Saturated KCl	-.836 -.854 -.829 -.821 -.818 -.815	0 1/2 1 1/2 2 1/2 3 1/2 4 1/2	Solution was stirred, and plate released gas vigorously and steadily during measurements. Following readings, plate was put in distilled water at room temperature; bubbling increased sharply.

<sup>a</sup>All potentials are recorded with reference to saturated-calomel electrode as zero at temperature of measurement.

<sup>b</sup>The operation of rinsing specimens and transferring them to potential-measuring apparatus took less than a minute. Therefore, zero (0) time for potential measurements was no more than 1 minute after removal of specimens from plating bath.

TABLE 1.- ELECTRODE POTENTIALS OF CODEPOSITED IRON-HYDROGEN PLATES - Continued

Experiment	Material measured and preparation	Temperature at which potential was measured, °C	pH	Electrolyte	Potential, v		Time of measurement, min	Remarks
					(a)	(b)		
19	Codeposited hydrogen-iron plate, prepared as in experiment 18	5	4.4	Saturated KCl	-0.850	0	Same as for experiment 18. At t = 14 min, rate of gas release had decreased somewhat, and a prominent green film of Fe(OH) <sub>2</sub> had formed. At end of measurements, pH = 4.6.	
					-0.828	1		
					-0.825	2		
					-0.822	3		
					-0.821	4		
-0.800	14							
20	Codeposited hydrogen-iron plate prepared as in experiment 18	5	10.3	Saturated KCl solution + NaOH	-0.845	0	Solution stirred. Readings were steady throughout, and plate bubbled vigorously during measurements. By end of measurements a little Fe(OH) <sub>2</sub> had formed on surface of plate. A sharp increase in bubbling occurred when plate was placed in distilled water at room temperature. During measurements, pH had changed to 9.7. This was due to absorption of CO <sub>2</sub> from dry-ice-acetone cooling bath.	
					-0.855	1		
					-0.864	2		
					-0.869	3		
					-0.873	4		
-0.878	14							
21	Pure-iron sample, surface cleaned	5	9.7	Saturated KCl solution + NaOH	-0.361	0, 1	Solution stirred. Readings steady.	
22	Codeposited hydrogen-iron plate prepared as in experiment 18, except that deposition temperature was 25° C. In addition, plate was washed, dried, and allowed to degas under dry ether for 10 min at 25° C. At end of this time, bubbling had stopped	5	9.6	Saturated KCl solution + NaOH	-0.640	0, 1	Solution stirred. Readings steady.	

<sup>a</sup>All potentials are recorded with reference to saturated-calomel electrode as zero at temperature of measurement.

<sup>b</sup>The operation of rinsing specimens and transferring them to potential-measuring apparatus took less than a minute. Therefore, zero (0) time for potential measurements was no more than 1 minute after removal of specimens from plating bath.

TABLE 1.- ELECTRODE POTENTIALS OF CODEPOSITED IRON-HYDROGEN PLATES - Continued

Experiment	Material measured and preparation	Temperature at which potential was measured, °C	pH	Electrolyte	Potential, v	Time of measurement, min	Remarks
					(a)	(b)	
23	Pure-iron sample	25	3.3	1.0 N FeSO <sub>4</sub> solution	-0.627 -.630 -.633 -.633	0 1 4 4½	Readings steady.
24	Codeposited iron-hydrogen plate Temperature of deposition bath, -30° C Plating time, 3 min Total current, 1 amp Platinum-cathode area, 2 sq in.	25	3.3	1.0 N FeSO <sub>4</sub> solution	-.776 -.762 -.755 -.750 -.746 -.740 -.736 -.734	0 1/2 1 1½ 2 3 4 4½	During readings, gas was being released continuously. Readings were steady. During washing prior to t = 0 plate appeared to have lost most of its hydrogen, since parts of plate were blown off during an initial vigorous release of gas.
25	Codeposited hydrogen-iron plate Temperature of deposition, -20° C Other conditions of preparation similar to those of experiment 24	25	3.3	1.0 N FeSO <sub>4</sub> solution	-.770 -.755 -.751 -.746 -.743 -.740 -.738 -.737	0 1/2 1 1½ 2 3 4 4½	Readings were steady. During measurements there was vigorous gas release, which decreased rapidly with time.
26	Codeposited iron-hydrogen plate Temperature of deposition, -10° C Other conditions as in experiment 24	25	3.3	1.0 N FeSO <sub>4</sub> solution	-.767 -.737 -.732 -.748 -.744 -.740 -.736 -.734	0 1/2 1 1½ 2 3 4 4½	Same as for experiment 25.

\*All potentials are recorded with reference to saturated-calomel electrode as zero at temperature of measurement.

<sup>b</sup>The operation of rinsing specimens and transferring them to potential-measuring apparatus took less than a minute. Therefore, zero (0) time for potential measurements was no more than 1 minute after removal of specimens from plating bath.

TABLE 1.- ELECTRODE POTENTIALS OF CODEPOSITED IRON-HYDROGEN PLATES - Concluded

Experiment	Material measured and preparation	Temperature at which potential was measured, °C	pH	Electrolyte	Potential, v		Time of measurement, min	Remarks
					(a)	(b)		
27	Codeposited iron-hydrogen plate Temperature of deposition, 0° C Other conditions as in experiment 24	25	3.3	1.0 N FeSO <sub>4</sub> solution	-0.763	0	Same as for experiment 25.	
					-.755	1/2		
					-.750	1		
					-.747	1 1/2		
					-.745	2		
					-.741	3		
-.738	4							
-.737	4 1/2							
28	Codeposited iron-hydrogen plate Temperature of deposition, 10° C Other conditions as in experiment 24	25	3.3	1.0 N FeSO <sub>4</sub> solution	-.765	0	Same as for experiment 25.	
					-.755	1/2		
					-.750	1		
					-.748	1 1/2		
					-.746	2		
					-.743	3		
-.740	4							
-.739	4 1/2							
29	Codeposited iron-hydrogen plate Temperature of deposition, 25° C Other conditions as in experiment 24	25	3.3	1.0 N FeSO <sub>4</sub> solution	-.754	0	Readings were steady. This plate, in contrast to those of experiments 24 to 28, released gas slowly during measurements.	
					-.752	1/2		
					-.749	1		
					-.748	1 1/2		
					-.747	2		
					-.746	3		
-.743	4							
-.742	4 1/2							

<sup>a</sup>All potentials are recorded with reference to saturated-calomel electrode as zero at temperature of measurement.

<sup>b</sup>The operation of rinsing specimens and transferring them to potential-measuring apparatus took less than a minute. Therefore, zero (0) time for potential measurements was no more than 1 minute after removal of specimens from plating bath.

TABLE 2.- ELECTRODE POTENTIAL OF COPPER HYDRIDE AS A FUNCTION OF pH  
 [Saturated-calomel-electrode scale, experiments 30 to 39]

System	Electrode potential, v																	
	pH = 2.0		pH = 2.6		pH = 2.95		pH = 3.3		pH = 4.0		pH = 4.5		pH = 5.5		pH = 5.7		pH = 6.0	
	Time initial <sup>a</sup>	Time final <sup>b</sup>	Time initial	Time final	Time initial	Time final	Time initial	Time final	Time initial	Time final	Time initial	Time final	Time initial	Time final	Time initial	Time final	Time initial	Time final
CuH(Pt) solution buffered	-----	-----	-0.052	-0.032	0.010	-0.010	-0.400	-0.070	-----	-----	-0.500	-0.330	-0.520 -0.560	-0.230 -0.210	-0.540	-0.350	-----	-----
CuH(Pt) solution unbuffered	-0.010	0.020	-----	-----	-----	-----	-----	-----	-0.030	-0.010	-----	-----	-----	-----	-----	-----	-0.083	-0.012

<sup>a</sup>Time initial refers to first potential reading taken after immersion of CuH slurry into electrolyte in which readings were taken.

<sup>b</sup>Time final refers to last potential reading taken. The elapsed time between initial and final readings varied from 15 min to 1 hr.



TABLE 3.- RESIDUAL HYDROGEN CONTENT AS A FUNCTION OF HYDROGEN ENTRY AND EXIT VARIABLES

Experiment	Preparation of sample	Bath (a)	Bath temperature, °F	Current density, amp/sq ft	Pickling time, min	$\Delta t$ , min (b)	Weight of sample, g	Amount of H <sub>2</sub> , ppm (c)	Remarks
40	No coating	A	86	110	10	1½	5.84	2.0	In none of the experiments was blistering or raising of the Pyseal surfaces observed, which would have been an indication of H <sub>2</sub> exit from the noncharged surfaces.
41	-----do-----	A	86	110	10	1½	5.58	3.6	
42	-----do-----	B	86	110	10	1½	5.56	4.3	
43	-----do-----	B	86	110	10	1½	5.75	2.5	
44	-----do-----	C	86	110	10	1½	5.72	2.1	
45	-----do-----	C	86	110	10	1½	5.89	3.4	
46	Pyseal on all but one 2-in. by 1/4-in. face	A	86	304	10	2½	5.66	.3	
47	-----do-----	A	86	304	10	2½	5.59	5.1	
48	Dry KCl and then Pyseal on all but one 2-in. by 1/4-in. face	A	86	304	10	2½	5.58	.9	
49	-----do-----	A	86	304	10	2½	5.77	1.3	

<sup>a</sup>See text for description of baths.

<sup>b</sup> $\Delta t$  was a measure of time elapsed between removal of sample from bath and its storage under mercury. The value was accurate within  $\pm 15$  sec.

<sup>c</sup>Precision of hydrogen analyses was  $\pm 0.2$  ppm, or  $\pm 10$  percent of reported value, whichever was greater in value. These analyses were carried out by the tin-fusion method (ref. 17).

TABLE 4.- DETERMINATION OF THE EFFECT OF DRY KCl AS AN EMERITMENT INHIBITOR

Experiment	Preparation of sample	Bath	Bath temperature, °C	Charging area, sq in.	Current density, amp/sq in.	Charging time, min	Δt, min (a)	Rockwell C and group	Ductility, bend angle, deg (b)	Thickness of sample, in. (c)	Remarks
50	Blank	—	—	—	—	—	—	44, A	98	0.0675	
51	Lucite cell + dry N <sub>2</sub>	A	86	0.5	0.80	10	4	44, A	57	.0675	
52	do	A	86	.5	.80	10	4	44, A	61	.0675 → 0.0665	
53	Lucite cell + dry KCl + dry N <sub>2</sub>	A	86	.5	.80	10	4	44, A	48	.0675 → 0.0665	KCl might have been wetted during run.
54	do	A	86	.5	.80	10	4	44, A	41	.0672 → 0.0665	KCl was not wetted during run.
55	Blank	—	—	—	—	—	—	42, B	175	.0675 → 0.0665	
56	Lucite cell + dry N <sub>2</sub>	A	86	.5	.80	10	4	42, B	88	.0675 → 0.0665	
57	Lucite cell + dry KCl + dry N <sub>2</sub>	A	86	.5	.80	10	4	42, B	66	.0675 → 0.0665	KCl was not wetted during run.
58	Lucite cell + dry N <sub>2</sub>	A	86	.5	.80	10	4	42, B	42	.0675 → 0.0665	
59	do	A	86	.5	.80	10	4	42, B	71	.0675 → 0.0665	
60	do	A	86	.5	.80	10	4	42, B	85	.0675 → 0.0665	
61	do	A	86	.5	.80	10	4	42, B	38	.0675 → 0.0665	
62	do	A	86	.5	.80	10	4	42, B	44	.0675 → 0.0665	
63	do	A	86	.5	.80	10	4	42, B	43	.0675 → 0.0665	
64	Lucite cell + dry KCl + dry N <sub>2</sub>	A	86	.5	.80	10	4	42, B	45	.0675 → 0.0665	KCl was not wetted during run.
65	do	A	86	.5	.80	10	4	42, B	68	.0675 → 0.0665	Do.
66	do	A	86	.5	.80	10	4	42, B	52	.0675 → 0.0665	Do.
67	do	A	86	.5	.80	10	4	42, B	40	.0675 → 0.0665	KCl possibly was wetted during run.
68	Blank	—	—	—	—	—	—	42, B	106	.0675 → 0.0665	
69	Lucite cell + dry N <sub>2</sub>	A	86	.5	.80	10	4	42, B	44	.0675 → 0.0665	
70	Blank	—	—	—	—	—	—	42, B	90	.0675	
71	Lucite cell + dry N <sub>2</sub>	A	86	.5	.80	10	4	42, B	70	.0675	
72	Lucite cell + dry KCl + dry N <sub>2</sub>	A	86	.5	.80	10	4	42, B	68	.0674	KCl was wetted during run.
73	Lucite cell + dry KCl + dry N <sub>2</sub>	A	86	.5	.80	10	4	42, B	46	.0674	KCl was not wetted during run.
74	Lucite was filled with distilled H <sub>2</sub> O	A + CS <sub>2</sub>	86	.5	.80	10	4	54	66	.064	Considerable blistering of cathode on charging surface occurred. No hydrogen was observed evolving from inner surface of sample during run.

<sup>a</sup>Estimated accuracy, ±3 sec.

<sup>b</sup>Estimated accuracy, ±5°.

<sup>c</sup>The arrow → between two thickness values refers to the fact that sample had been electropolished before charging. The bath used was 50 percent concentrated chemically pure H<sub>2</sub>SO<sub>4</sub> by volume plus 50 percent chemically pure H<sub>3</sub>PO<sub>4</sub> (85 percent) by volume. Current density was about 2 amp/sq in.; bath temperature was about 25° C.

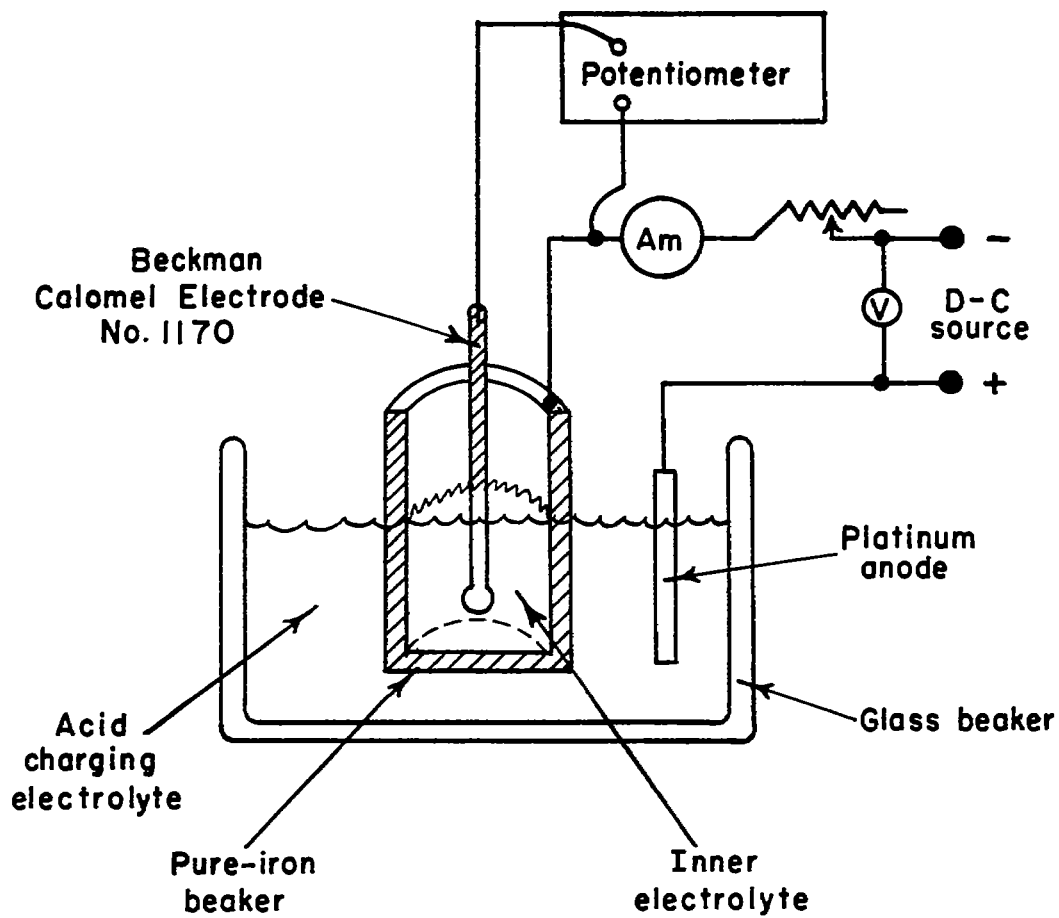


Figure 1.- Apparatus for measuring transmitted electrode potentials.

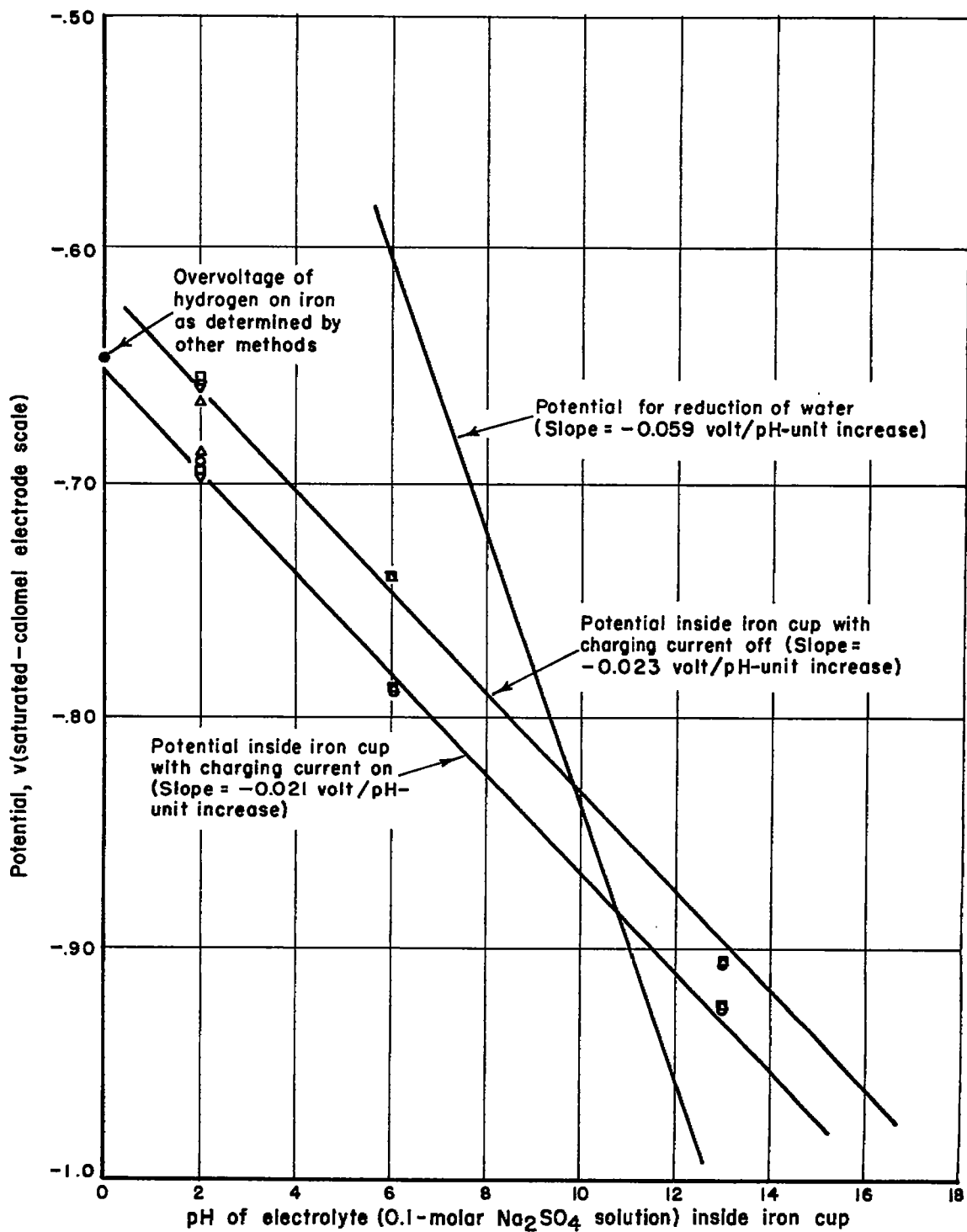


Figure 2.- Potential measurements on inside of pure-iron cup during and after cathodic charging. No  $\text{H}_2$  gas was evolved on inside of cup during measurements with current either on or off. No arsenic was in the charging electrolyte.

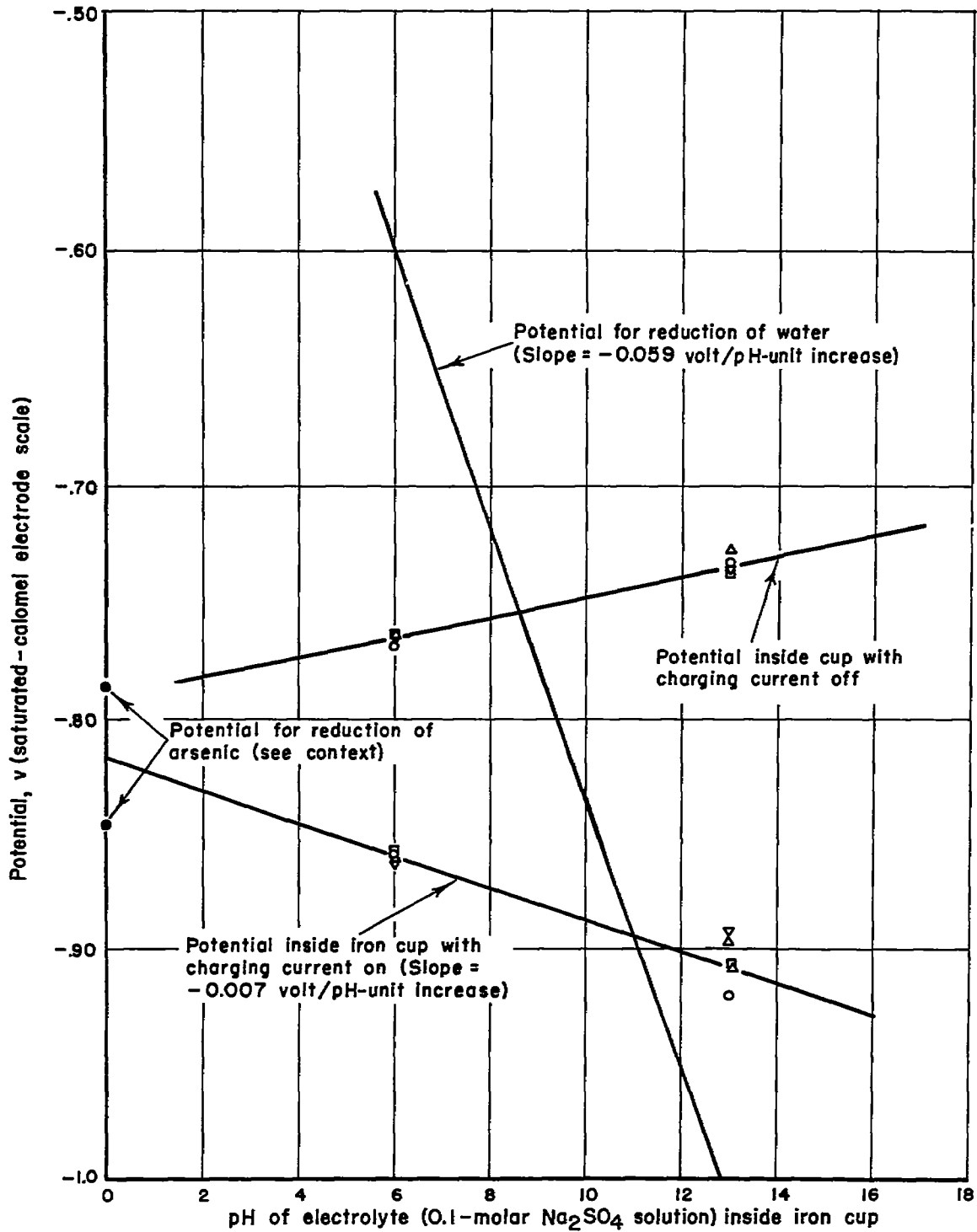


Figure 3.- Potential measurements on inside of pure-iron cup during and after cathodic charging. During all readings, current on or off,  $\text{H}_2$  was being evolved inside cup at an appreciable rate. Arsenious acid was in the charging electrolyte.

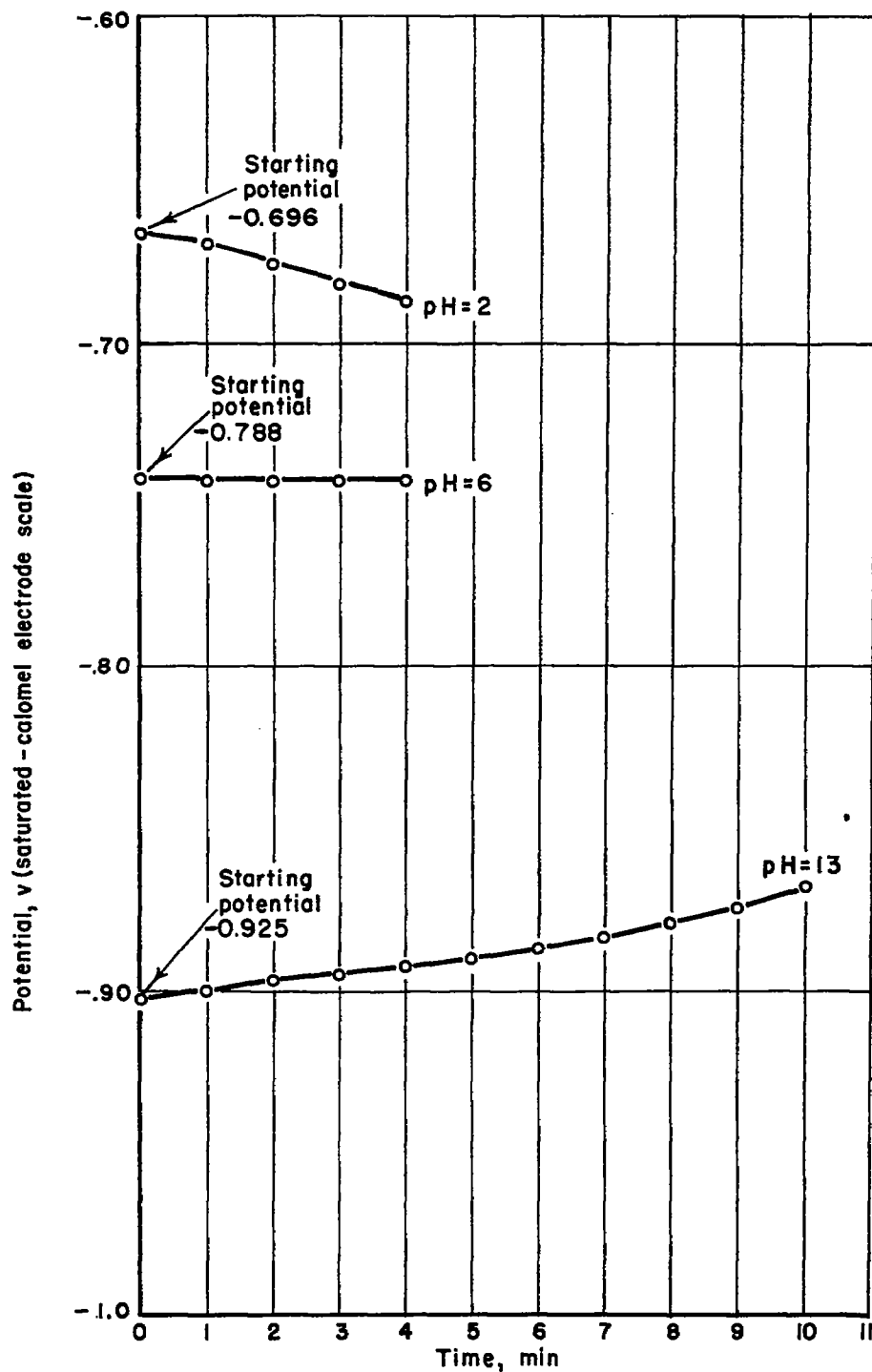


Figure 4.- Potential versus saturated-calomel electrode as a function of time for inside of iron cup with current off following 20-minute charging period. Charging bath, 2 percent  $H_2SO_4$  (by volume) only. (Zero time indicates first measurement made after opening circuit; closed circuit potential is indicated as starting potential.)

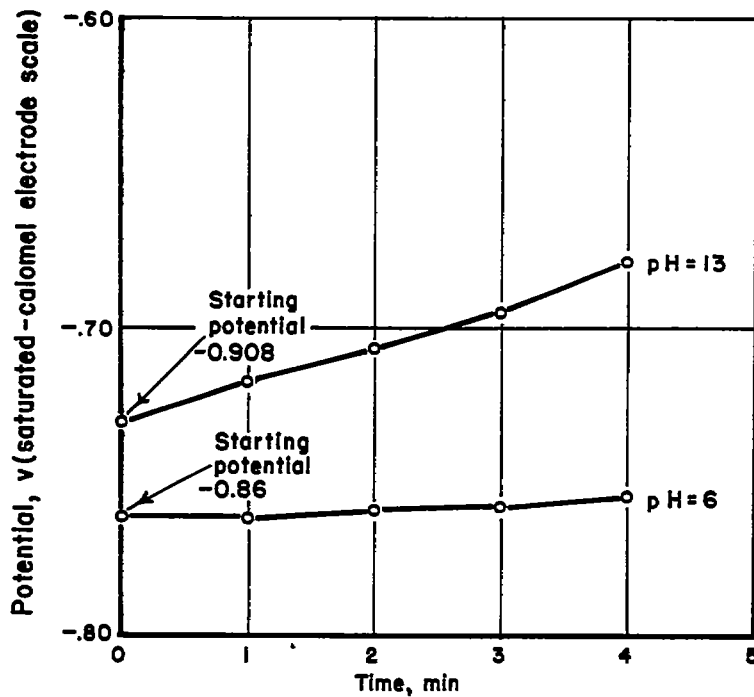
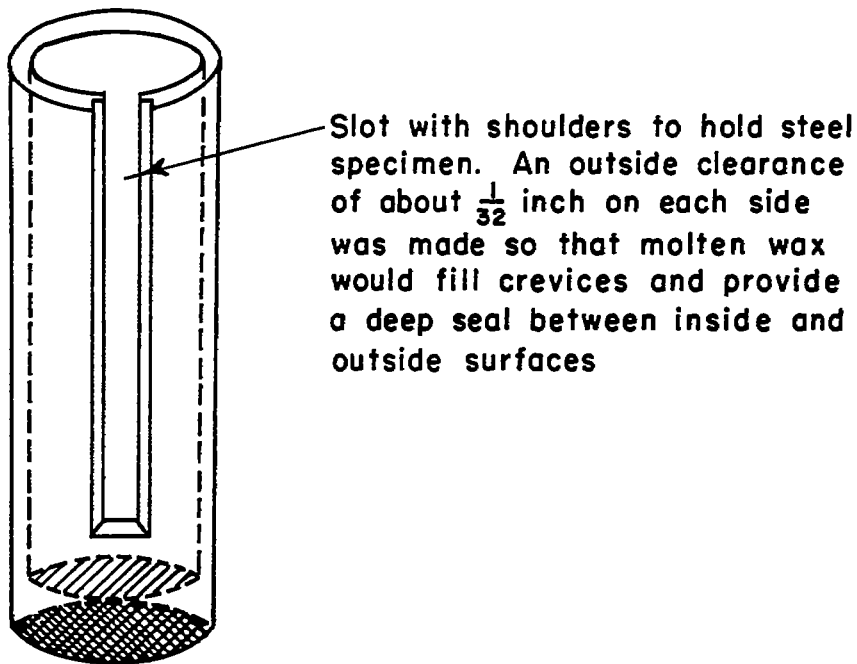


Figure 5.- Potential versus saturated-calomel electrode as a function of time for inside of iron cup with current off following 20-minute charging period. Charging electrolyte, 2 percent  $H_2SO_4$  (by volume) with sodium arsenate.



Solid Bottom

Figure 6.- Lucite holder for electrolysis of SAE 4130 steel specimens.