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DETERMINATIONS OF HYDROGEN IN FERROUS MATERIALS BY VACUUM EXTRACTION AT 800° C AND BY VACUUM FUSION

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ABSTRACT

Determinations of hydrogen in a variety of ferrous materials were made by vacuum extraction at 800° C and by vacuum fusion. The warm extraction method has the advantages of rapid operation and relative freedom of the evolved hydrogen from association with other gases. A high hydrogen content produced by heating in hydrogen at high temperature, or by electrolysis, is unstable at room temperature, but the hydrogen contents of commercial steels, after hot working and storage, were low and stable, and without segregation. Steels with high chromium contents dissolve more hydrogen and retain it more tenaciously than do plain carbon or low-alloy steels.

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I. INTRODUCTION

The presence of hydrogen as a possible constituent of ferrous materials has been recognized since 1863, when Deville and Troost [1]¹ published their results on the diffusion of hydrogen through iron. Three years later Graham [3] reported that meteoric iron evolved gases, chiefly hydrogen, when it was heated in a vacuum. Cailletet [2] obtained similar results, but a lack of reproducibility in his experiments led him to abandon the investigation. In the ensuing years the significance of the presence of hydrogen in ferrous materials has been widely discussed, with reference to such phenomena as the porosity of ingots; blistering of sheet metal; hardness and brittleness of electrodeposits; embrittlement during pickling; deterioration of steels in high-pressure reactions, as in the synthesis of ammonia; and particularly with reference to the development of the defects known as "shatter cracks" in railroad rails and "flakes" in forgings. In a current review entitled "Hydrogen, Flakes and Shatter Cracks," Zapffe and Sims [21] record the accumulation of a bibliography of 500 references on this subject alone.

In contrast to this voluminous literature on the sources, presence, and effects of hydrogen in ferrous materials, information about its

¹ Figures in brackets indicate the literature references at the end of this paper.

quantitative determination in such material is scanty indeed. Most of the information on the effects of hydrogen has been obtained by indirect methods rather than by direct analysis of individual specimens. For instance, the effects on the properties have been identified as effects of hydrogen, mainly by a comparison of the behavior of duplicate specimens, one of which had been intentionally exposed to hydrogen at some stage in its history. The lack of information about the direct, quantitative determination of hydrogen can be attributed largely to the very small amounts of hydrogen, less than 0.001 percent by weight, that are present in ordinary ferrous materials. Such amounts of any constituent usually are considered to be too insignificant to justify the time and labor that are required for their quantitative determination, and they are generally reported only in "rounded" figures or as "traces." This was the status of the determination of hydrogen until recent interest in the relation of hydrogen to the phenomenon of flaking in steel, particularly since the publication in 1935 of the work of Bennek, Schenck, and Müller [9], showed the need for accurate determinations of amounts considerably less than 0.001 percent.

Most of the determinations of hydrogen which have been reported have been obtained by extraction of hydrogen from the specimen in a vacuum at temperatures either above or below the melting point of the specimen. The vacuum fusion method has been used for approximately 20 years for estimations of hydrogen in conjunction with determinations of oxygen and nitrogen. This method, although satisfactory for the determination of amounts of oxygen and nitrogen present ordinarily in steel, has not been sufficiently accurate for the determination of 0.001 percent or less of hydrogen. Chipman and Fontana [10] in 1935 reported that duplicate determinations of hydrogen might differ by as much as 0.0005 percent. In the cooperative study of methods for the determination of oxygen in steel [13] in 1937, four of the cooperators reported results for hydrogen by vacuum fusion. These results indicated that the hydrogen content of each of the eight selected steels was less than 0.001 percent, but a more accurate value could not be indicated. For example, the results for one steel ranged from 0.00005 to 0.00050 percent of hydrogen and for another from 0.00002 to 0.00060 percent. Agreement of the results of four analysts within 0.001 percent is highly satisfactory for general analysis, but leaves much to be desired when significant amounts may be only 0.0001 or 0.0002 percent. Obviously, an increase in precision and a decrease in the blank correction of the vacuum fusion method were desirable for the determination of hydrogen, and some progress along these lines has been made since 1937. Sloman [18] described a vacuum fusion apparatus in which the hydrogen blank was so low that it could be ignored.

Most of the determinations of hydrogen by vacuum fusion have involved inductive heating of the specimen, but Meyer and Willems [14] and Newell [22] have described graphite spiral furnaces for vacuum fusion, in which the blank was low enough to permit satisfactory determinations of hydrogen. Newell reported that the blank for his apparatus did not exceed 0.00005 g of hydrogen per hour.

One difficulty in the determination of hydrogen by vacuum fusion is that the volume of carbon monoxide and nitrogen evolved is much

greater than the volume of hydrogen. The problem then is to determine a small amount of hydrogen in the presence of large amounts of carbon monoxide and nitrogen. However, Graham's [3] observation, that the gas evolved from solid iron by vacuum extraction at red heat was chiefly hydrogen, suggested the possibility of the determination of hydrogen in hydrogen-rich mixtures. This observation was confirmed by experiments of other investigators, which showed that hydrogen diffuses readily through solid steel at moderately elevated temperatures, whereas the diffusion of oxygen and nitrogen under these conditions is relatively slow.

The vacuum extraction of hydrogen at relatively low temperatures was developed into an analytical method by Körber and Ploum [6]. Their preferred temperature for the extraction was 400° C. They referred to their method as a "hot extraction" method, but, inasmuch as this term has been applied to the vacuum fusion method, which operates at temperatures above the melting point of iron, it seems desirable to identify the lower temperature method as a "warm extraction" rather than a "hot extraction."

Körber and Ploum used the warm extraction method to measure the hydrogen contents of ferrous specimens after pickling in acid and after cathodic charging by electrolysis. Bardenheuer and Ploum [8] studied the hydrogen embrittlement of ferrous specimens. Sloman [18] determined hydrogen in cylindrical specimens about 1 cm in diameter, at 650° to 700° C, and decided that 1 to 2 hours was required for complete extraction. The amounts of hydrogen extracted from different specimens ranged from a trace to about 0.00050 percent, and the values were in excellent agreement with values obtained by vacuum fusion in an apparatus for which the hydrogen blank was so low that it could be ignored. Newell [22] found that 600° C was a satisfactory temperature for the extraction of hydrogen from ferrous specimens, but that certain aluminum alloys did not give off their hydrogen until they were actually molten.

Two other methods, in addition to the vacuum fusion and warm extraction methods, have been proposed for the determination of hydrogen. Moreau, Chaudron, and Portevin [11] found that hydrogen and other gases could be removed from metallic specimens by ionic bombardment in an evacuated tube. This "cold" extraction was particularly applicable to surface films of gas, or to very thin specimens, but thicker specimens could be heated by induction to increase the rate of hydrogen elimination. However, the results for hydrogen in iron obtained by this method were not in good agreement with those obtained by other procedures. The other method, which was described by Schwartz and Guiler [20], involves direct combustion of the finely divided sample in oxygen, with subsequent collection of water in a phosphorus pentoxide tube. Results for the hydrogen contents of some samples of steel and ingot iron were of the same magnitude as those obtained by vacuum fusion.

The investigation reported in this paper was undertaken to study the applicability of the vacuum fusion and warm extraction methods to the determination of hydrogen in ferrous materials and to determine the accuracy of both methods, either by analysis of samples of known hydrogen content or by agreement in results of determinations on the same sample by both methods.

II. APPARATUS

The vacuum fusion apparatus and procedure were essentially as described by Vacher and Jordan [5], although split graphite radiation screens had been substituted for mullite screens, a three-stage high-capacity diffusion pump and enlarged connections to the furnace had been installed to permit more rapid removal of gas, and the absorption of gas was measured by means of the changes in pressure in the analytical train, rather than by weighing an absorption tube.

In the usual operation of this vacuum fusion apparatus for the determination of oxygen and nitrogen, the empty crucible is outgassed at about 1,800° C until the pressure in the furnace does not exceed 8×10^{-4} mm of mercury. This requires outgassing for 1 to 2 hours. When the temperature of the crucible is subsequently lowered to the operating temperature, 1,625° C, the pressure in the furnace drops to the "base pressure" of not more than 1×10^{-4} mm of mercury. A sample is dropped into the hot crucible, and the extraction of gases from the sample usually is completed in about 15 minutes. The furnace is then shut off from the analytical train, and the evolved gases are circulated through a copper oxide furnace and absorption train. Analysis of the gas mixture requires 30 to 45 minutes, after which the train is again connected to the furnace and another determination started. The size of the samples for vacuum fusion is limited by the storage capacity of the apparatus for the total volume of evolved gases. The usual weight of sample is between 10 and 20 g, but smaller samples must be used if the gas content is high.

In the routine operation of the apparatus, when the furnace is outgassed for 1 or 2 hours, the blank correction for oxygen and nitrogen is low enough to permit satisfactory determinations of ordinary amounts of these constituents. The hydrogen blank is less than the blanks for either oxygen or nitrogen, but still is too high and too irregular to be satisfactory, because the amount of hydrogen to be determined is so small. It was found that extension of the outgassing period decreased the size and variability of the blank until, with 6 to 8 hours of outgassing, the blank correction for 15 minutes was between 0.00002 and 0.00004 g of hydrogen, which is equivalent to 0.00002 to 0.00004 percent of hydrogen in the analysis of 10-g samples. Outgassing for 6 to 8 hours made the determination an extremely tedious affair, but seemed to be necessary if this vacuum fusion apparatus was to be used for the determination of hydrogen. The blank from the 1- or 2-hour outgassing period varies between 0.000006 and 0.000015 g of hydrogen, which permits determinations of satisfactory precision to be made only when the hydrogen content of the sample is high, as in cathode electrolytic iron, which may contain 0.0015 percent or more of hydrogen.

The apparatus for the determination of hydrogen by warm extraction is shown diagrammatically in figure 1. A specimen is suspended on a fine Nichrome wire in a vertical quartz tube, $1\frac{1}{4}$ inches in diameter and 10 inches long, which constitutes the furnace tube. Initial evacuation is attained in 5 minutes, by means of a rotary oil pump connected at *B*. When the pressure in the furnace has been reduced to about 0.01 mm of mercury, the oil pump connection is closed at *B* and opened at *C*, so that the furnace tube is evacuated for a second 5-minute period, to about 0.0001 mm, by means of the rotary pump and a mercury diffusion pump in series. The specimen within the

furnace tube is then heated rapidly to the desired temperature by means of a high-frequency induction coil which is connected to a 3-kva oscillator. The gases evolved from the sample are removed from the furnace by means of the mercury diffusion pump. When all of the gas has been transferred to the storage system, the furnace is shut off, and the accumulated gas is circulated through a tube containing hot copper oxide and then through an absorption tube which contains anhydrous magnesium perchlorate. The volume of hydrogen in the evolved gas is indicated by the decrease in pressure which accompanies the absorption of water vapor.

Successful operation of the method depends upon the outward diffusion of hydrogen from solid steel. Consequently the thickness of the specimen, the temperature to which it is heated, and the time

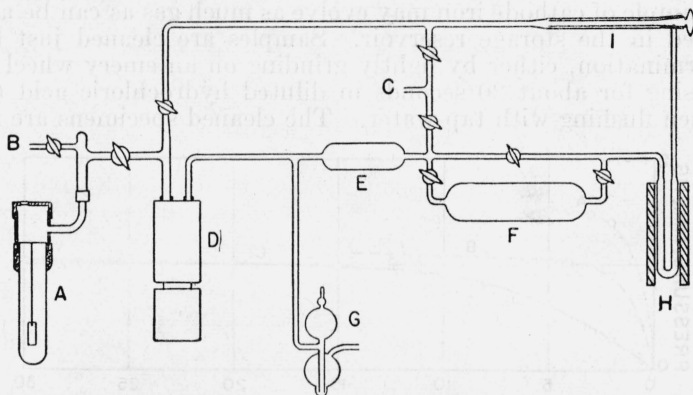


FIGURE 1.—Apparatus for the determination of hydrogen by vacuum extraction at 800° C.

A, Furnace tube; B, connection to oil pump or to air; C, connection to oil pump; D, mercury diffusion pump; E, reservoir; F, auxiliary reservoir; G, McLeod gage; H, copper oxide tube and furnace; and I, absorption tube filled with anhydrous magnesium perchlorate.

required for complete extraction are interrelated. Pihlstrand's data [15] show that the higher the temperature and the thinner the specimen, the less is the time required for complete extraction of hydrogen. However, the temperature and dimensions of the specimen should be adjusted with respect to the size of the furnace tube so that the walls do not become appreciably warm during a run.

An operating temperature of about 800° C, determined by visual inspection of the sample and by occasional pyrometric observations, was selected. Six minutes at this temperature was found to be ample for the extraction of gases from specimens up to 5 mm in thickness, and 15 minutes was enough for specimens between 5 and 13 mm in thickness. Figure 2 shows the rate of evolution of gas from specimens of different thicknesses. A blank correction was applied to each of the observed pressure values, so that each of the plotted points represents the pressure (or amount) of gas evolved from the specimen. Each of the curves rises rapidly at first and then tapers off to a constant value, which represents complete extraction. A constant pressure is not obtained in an actual run where the continuous evolution of blank gas causes the pressure to increase continuously, even after all of the gas has been extracted from the sample. The fact that extraction of gas from a sample 13 mm thick was so nearly

complete in 15 minutes is in agreement with the calculations of Pihlstrand [15] and the observations of Newell [22]. An extraction period of 1 or 2 hours, as recommended by Sloman [18], seems to be unnecessarily prolonged, even though Sloman's extraction temperature was only 650° to 700° C.

The gases which are collected in the analytical train consist largely of hydrogen. Analysis of a number of gas mixtures showed that the proportion of hydrogen in the evolved gas varied from 50 or 60 percent to as high as 80 or 90 percent, depending upon the previous history and hydrogen content of the specimen.

The optimum size of sample depends upon its hydrogen content and to some extent upon its shape, but samples up to 40 g in weight have been treated successfully in the apparatus. On the other hand, a 5-g sample of cathode iron may evolve as much gas as can be accommodated in the storage reservoir. Samples are cleaned just before a determination, either by lightly grinding on an emery wheel or by immersing for about 20 seconds in diluted hydrochloric acid (2+1) and then flushing with tap water. The cleaned specimens are rinsed

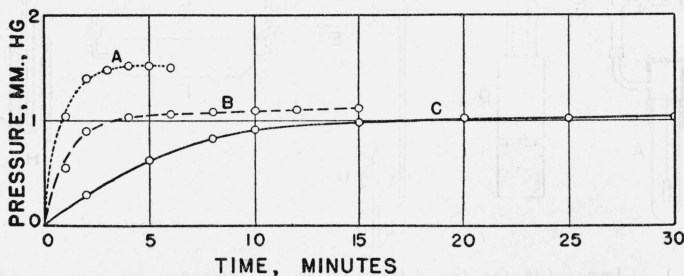


FIGURE 2.—Rate of evolution of gas at 800° C from specimens of different thicknesses.

A, Specimen 4 mm thick with high content (0.0016%) of hydrogen; B, specimen 5 mm thick with moderate content (0.00037%) of hydrogen; and C, specimen 13 mm thick with moderate content (0.00031%) of hydrogen

with alcohol and dried with ether. In repeated determinations on the same specimen, the results were not affected by the method of cleaning. Light grinding is preferred for most of the specimens, but pickling is more convenient if the surface is rough or irregular.

The blank correction for the apparatus was determined by duplicating the conditions of an actual run, except that an outgassed sample from a previous run was used instead of fresh material. The outgassed sample was exposed to the air between determinations and was cleaned and washed just before the determination. Consequently, the blank correction included any gas or moisture that may have been adsorbed on the surface of the sample. To minimize the effect of variations in atmospheric humidity, the air that was admitted to relieve the vacuum in the furnace before it was opened for admission of a specimen was dried by passing through anhydrous magnesium perchlorate.

The hydrogen blank for this apparatus is of the order of 0.000007 g of hydrogen for a 15-minute run. This is only slightly larger than the best hydrogen blanks for the vacuum fusion apparatus, which were obtained by extended outgassing at high temperatures. Some variation of the blank for the warm extraction apparatus was observed at different seasons of the year. For example, during the humid

summer months the blank amounted to about 0.000010 g for a 15-minute run, whereas in winter operation the blank might be as low as 0.000005 g. Blank determinations made on the same day agreed within ± 0.000001 g, so that one blank determination per day was all that was necessary in a series of similar samples. The size of the samples, from 5 to 40 g, did not affect the blanks beyond the range of seasonal variations. The results of several analyses showed that hydrogen constituted 25 to 35 percent of the blank gases.

III. DETERMINATIONS OF HYDROGEN BY WARM EXTRACTION AND BY VACUUM FUSION

Determinations of hydrogen in a variety of materials showed that the results by both methods were in good agreement whenever the hydrogen content was high and stable. For example, the hydrogen content of a piece of cathode iron was 0.0014 percent by vacuum fusion and 0.0015 percent by warm extraction. The reproducibility of results by each method in the determination of such amounts of hydrogen, judged by the agreement in repeated determinations by the same method, was about ± 0.0001 percent. This variation was considerably greater than that of the blank correction for either method, but the over-all precision of each determination was good enough for the determination of these amounts of hydrogen. The agreement in results by two methods furnishes some evidence of the accuracy of both methods, at least for the determination of relatively high hydrogen contents.

When attention was turned to the analysis of steels with lower hydrogen contents, 0.0001 percent or less, the agreement in results was not so satisfactory. Results of determinations by vacuum fusion usually were somewhat higher and decidedly more variable than those obtained by warm extraction. For example, a series of determinations on a rod of ingot iron yielded values from 0.00000 to 0.00028 percent, with an average of 0.00018 percent by vacuum fusion, whereas values by warm extraction ranged only from 0.00000 to 0.00003, with an average of 0.00002 percent. In a sample of low-carbon steel, determinations by vacuum fusion ranged from 0.00006 to 0.00015, with an average of 0.00012, whereas the range of determinations by warm extraction was 0.00003 to 0.00007, with an average of 0.00004 percent. In determinations on a number of simple steels, duplicate determinations by warm extraction usually were within the range of ± 0.00001 percent and seldom were as far apart as ± 0.00002 percent, whereas duplicate determinations by vacuum fusion usually were within the range of ± 0.00005 percent but occasionally varied as much as ± 0.00015 percent.

Evidently the over-all precision of the vacuum fusion procedure is less than that of the warm extraction procedure although the vacuum fusion blank is the lower and more precise. The lack of precision in the vacuum fusion determinations, in spite of the low blank correction, can hardly be an indication of segregation of hydrogen in the sample material, in view of the precision obtained with the warm extraction method when using the same sample material. A plausible explanation of the lack of precision in the vacuum fusion determinations lies in the uncertainty that is inherent in the procedure used for the analysis of the gas mixture. This procedure depends upon determinations of the differences in pressure which accompany the absorp-

tion of hydrogen in the form of water vapor from the gas mixture. If the amount of hydrogen, or the proportion of hydrogen in the gas mixture, is large, the changes in pressure which accompany the absorption will be appreciable and can be determined with reasonable precision. But if the amount of hydrogen is small, and particularly if the small amount of hydrogen is diluted with large amounts of oxygen and nitrogen, then the determination of hydrogen requires accurate readings of very small changes in large volumes (or pressures). Confirmation of this hypothesis is found in the fact that the least precise results were obtained in analysis of materials, such as ingot iron or high-nitrogen steel, in which the total gas content limited the size of the sample, and thus limited the amount of hydrogen that was to be determined in the presence of large amounts of oxygen or nitrogen. Revision of the analytical procedure, perhaps with the substitution of gravimetric for pressuremetric determinations of hydrogen, probably would improve the precision of the determination, but, because of the success achieved with the warm extraction method, this revision was not attempted.

The precision of the warm extraction method appeared to be satisfactory for the determination of both high and low hydrogen contents, and its accuracy was indicated for high hydrogen contents by agreement with results by vacuum fusion. Some indication of the accuracy, as well as the precision, of determinations of low hydrogen contents by warm extraction was desired, and, in the absence of an independent method for check determinations, attention was turned to the possibility of preparing standard samples, that is, samples of known hydrogen contents.

Data for the solubility of hydrogen in solid iron at elevated temperatures have been reported by several investigators [4, 7, 16]. These data suggested the possibility of preparing specimens with known and determinable hydrogen contents by rapidly quenching specimens which had been saturated with hydrogen at elevated temperatures. Accordingly, thin slabs of remelted electrolytic iron were prepared, 2 to 5 mm in thickness and usually between 15 and 20 g in weight. Each of these specimens was held for 1 hour at a definite temperature in an atmosphere of hydrogen and was then quenched in water, cleaned, dried with alcohol and ether, and analyzed at once for hydrogen. The extraction of hydrogen for the analytical determination usually was started within 30 minutes of the beginning of the quenching operation.

A comparison of the results of these experiments with the solubility data [4, 7, 16] is shown in figure 3. Both curves show that the solubility of hydrogen increases with increasing temperature and that there is an abrupt change in solubility in the region of the A_3 transformation. However, the determinations on the quenched specimens invariably are less than the values from the solubility curve, and the divergence of the two curves increases with increasing temperature. At 800° C approximately 80 percent of the theoretical amount of hydrogen is recovered from the quenched specimen, but at 1,200° C the recovery is only about 75 percent. Similar results have been obtained by Bardenheuer and Ploum [8], and their inability to obtain 100-percent recovery was ascribed to failure of the sample to retain the theoretical amount of hydrogen until the analysis was started. The quench is not instantaneous and the diffusion of hydrogen at

elevated temperatures is rapid. Bardenheuer and Ploum showed that the surface layers of quenched specimens contained less hydrogen than did the interior. Undoubtedly some hydrogen is lost from the specimen while it is cooling during the quench, and experiments showed that further losses of hydrogen from quenched specimens may occur during storage at room temperature. Under these conditions, recoveries of 75 to 80 percent of the theoretical amounts of hydrogen probably represent 100-percent recovery of the hydrogen contents of the sample at the time the analysis was made.

Several experiments demonstrated the loss of hydrogen from quenched specimens during storage at room temperature, as has been reported by other observers [8, 12, 19]. For example, analysis of a

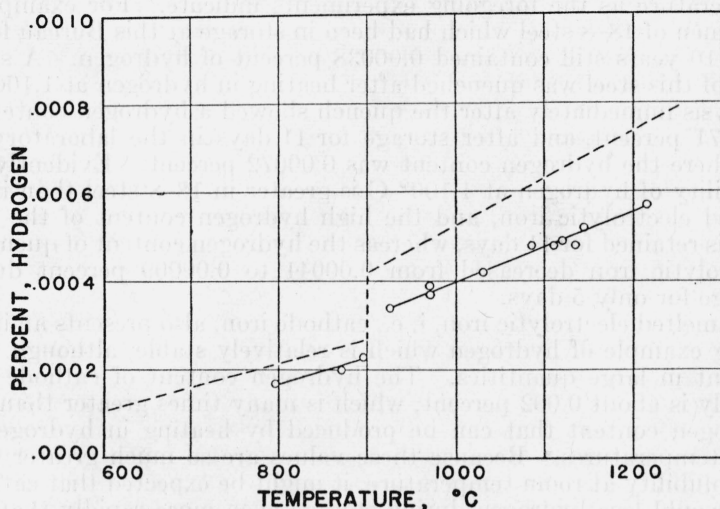


FIGURE 3.—Determinations of hydrogen in specimens of remelted electrolytic iron quenched after saturation with hydrogen at elevated temperatures.

The dashed line shows the solubility of hydrogen in iron at various temperatures, as reported in the literature [4, 7, 16].

portion of a specimen immediately after the quench showed a hydrogen content of 0.00041 percent. The rest of the specimen, which was 7 mm thick, was exposed to the laboratory atmosphere. After 2 days the hydrogen content had decreased to 0.00015 percent and after 5 days it was only 0.00009 percent. The latter value approaches the theoretical solubility at room temperature. Additional experiments showed that the loss of hydrogen from quenched specimens at room temperature is intensified by storage in a vacuum. For example, storage for 4 hours in a vacuum after 1 hour in the air lowered the hydrogen content of a specimen from 0.00049 to 0.00026 percent, approximately the loss that would occur in 24 hours of storage in the atmosphere. However, no appreciable loss could be detected during short periods of evacuation, such as are used in the operation of low-temperature extraction apparatus. When the furnace was evacuated for 5 minutes before heating the specimen, a value of 0.00049 percent of hydrogen was obtained; and when the preliminary evacuation was continued for 15 minutes, a value of 0.00048 percent was obtained.

These experiments indicate that the major loss of hydrogen from the specimen occurs during the quench and that the subsequent loss will not be serious when analysis is made by the warm extraction method. However, it is evident that the determination of hydrogen should be completed as rapidly as possible. For example, determinations by the vacuum fusion procedure with the long outgassing period invariably yielded values of about 0.00010 percent, regardless of the temperature at which the specimen was saturated with hydrogen before quenching. Evidently most of the hydrogen in excess of the solubility at room temperature is lost during the long outgassing which is necessary to bring the blank correction down to a suitably low and constant figure.

However, hydrogen does not always diffuse as rapidly at room temperature as the foregoing experiments indicate. For example, a specimen of 18-8 steel which had been in storage at this Bureau for at least 10 years still contained 0.00038 percent of hydrogen. A specimen of this steel was quenched after heating in hydrogen at 1,100° C. Analysis immediately after the quench showed a hydrogen content of 0.00071 percent, and after storage for 11 days in the laboratory atmosphere the hydrogen content was 0.00072 percent. Evidently the solubility of hydrogen at 1,100° C is greater in 18-8 steel than in remelted electrolytic iron, and the high hydrogen content of the 18-8 steel is retained for 11 days, whereas the hydrogen content of quenched electrolytic iron decreased from 0.00041 to 0.00009 percent during storage for only 5 days.

Unmelted electrolytic iron, i. e., cathode iron, also presents an interesting example of hydrogen which is relatively stable, although it is present in large quantities. The hydrogen content of cathode iron usually is about 0.002 percent, which is many times greater than any hydrogen content that can be produced by heating in hydrogen at high temperatures. Because these values are so much greater than the solubility at room temperature, it might be expected that cathode iron would lose hydrogen during storage even more rapidly than the quenched specimens, but this is not the case. As a matter of fact, the hydrogen content of cathode iron is stable enough so that accurate analyses, in agreement with results by warm extraction, can be made by vacuum fusion, even with the 6- to 8-hour outgassing period. However, the hydrogen content of cathode iron is not entirely stable, even though the loss during storage at room temperature is much less than that of quenched iron of the same composition. Analyses of portions of the same piece of cathode iron, over a period of 2 years, gave the following results:

	<i>Percent</i>
June 1938.....	0. 0022
January 1939.....	. 0018
June 1939.....	. 0016
September 1939.....	. 0014
June 1940.....	. 0013

It is well known that the hydrogen content of cathode iron is unstable at elevated temperatures, i. e., hydrogen is readily removed from cathode iron by annealing or heating in a vacuum, as in the warm extraction method of analysis. It is interesting to note that cathode iron, which originally contained about 0.002 percent of hydrogen, contained only 0.00045 percent after it had been heated in hydrogen at 1,100° C and then quenched.

In other experiments the hydrogen was extracted from specimens of remelted electrolytic iron by heating in vacuum at 800° C. The specimens were then charged with hydrogen by electrolysis, to see what hydrogen contents could be produced in this manner. The electrolyte was dilute sulfuric acid (0.1 *N*), and the anode was a piece of platinum gauze. With current densities of 0.01 to 0.02 amp/cm² of cathode surface, electrolysis for 2 to 4 hours produced hydrogen contents of the order of magnitude of that of electrodeposited iron and greatly in excess of the solubility values. These hydrogen contents, however, are much less stable than that of electrodeposited iron. For example, the piece of electrodeposited iron cited in a preceding paragraph still retained 0.0013 percent of hydrogen after 2 years' storage, whereas the hydrogen content of a piece of cathodically charged iron dropped from 0.0030 to 0.0002 percent in 11 days.

Electrodeposition evidently can produce hydrogen contents that are greatly in excess of the solubility value, when the hydrogen is deposited on the smooth surface of a solid piece of iron as well as when hydrogen and iron are codeposited, but the mechanism by which these high hydrogen contents are achieved is not clear. It is generally assumed that the hydrogen in electrodeposited iron may be present as molecular gas in cavities and discontinuities in the structure of the iron, as atomic hydrogen which is piled up beyond the ordinary solubility values, or as water or iron hydroxide which has been mechanically entrapped during the deposition of the iron. The hydrogen contents of cathodically charged specimens should consist chiefly of atomic hydrogen. The hydrogen contents of electrodeposited iron and of cathodically charged specimens of iron may be approximately the same, but the hydrogen in the former is more stable than in the latter. This suggests the presence of hydroxides or of structural discontinuities filled with molecular hydrogen in electrodeposited iron. If structural discontinuities in the metal are filled with molecular hydrogen by combination of diffused hydrogen atoms, and if this hydrogen is removed by warm extraction, it might be possible to refill the voids by extended heating in hydrogen. This, however, could not be done with either moist or dry hydrogen. In no case was a hydrogen content in excess of the solubility value produced in electrodeposited iron or in any other iron by heating in hydrogen. The only conclusions that can be drawn from these experiments are that high hydrogen contents can be produced by electrolytic action, but the hydrogen in electrodeposited iron is present in a form different from that of an equal amount of hydrogen in a cathodically charged specimen.

IV. HYDROGEN CONTENTS OF SIMPLE STEELS

After the reliability of the warm extraction method had been investigated, attention was turned to the determination of the hydrogen contents and possible segregation of hydrogen in steels of commercial origin. The sample material consisted of sections of the rods of ingot iron and seven low-carbon steels which were used in the cooperative study of methods for the determination of oxygen [13].

Determinations of hydrogen by extraction at 800° C were made on specimens taken at 10-foot intervals along the length of each of the 1-inch-diameter rods. Disks $\frac{1}{4}$ and $\frac{1}{2}$ inch thick were cut from the rods at appropriate locations, and a sample for analysis consisted of

a half disk $\frac{1}{2}$ inch thick or both halves of a $\frac{1}{4}$ -inch disk. Extraction at 800°C was continued for 15 minutes. The results of these determinations are shown in table 1.

The determinations on samples from different points along a rod invariably were in as good agreement as was obtained for adjacent samples from the same location or for two halves of the same disk. There was no evidence of longitudinal segregation of hydrogen in these rods, and a few determinations on shell and core samples failed to reveal any evidence of transverse segregation.

TABLE 1.—*Distribution of hydrogen in long rods of steel*

Location from end of rod	Hydrogen in steel—							
	1	2	3	4	5	6	7	8
<i>ft</i>	%	%	%	%	%	%	%	%
20.....	0.00002	0.00000	0.00003	0.00001	0.00001	0.00001	0.00001	0.00004
30.....	.00002	.00001	.00004	.00003	.00001	.00002	.00000	.00004
40.....	.00003	.00003	.00004	.00001	.00001	.00003	.00002	.00005
50.....	.00001	.00000	.00002	.00002	.00002	.00003	.00002	.00003
60.....	.00001	.00001	.00005	.00004	.00003	.00003	.00001	.00006
70.....	.00003	.00000	.00004	.00002	.00002	.00002	.00003	.00003
80.....	.00003	.00002	.00003	.00000	.00004	.0000300004
Average.....	0.00002	0.00001	0.00004	0.00002	0.00002	0.00002	0.00001	0.00004

Steels 3 and 8 appeared to have slightly higher hydrogen contents than the others but the difference was slight. Apparently the hydrogen content of each of these rods was determined by the previous history of heat treatment and hot working rather than by minor differences in composition. It is interesting to compare these results with the limited data for hydrogen that were available in the 1937 report on the determination of oxygen. The present data consist entirely of small values in the fifth decimal place, whereas the earlier determinations range up to large values in the fourth decimal place. The uniformly low and consistent results by warm extraction demonstrate the precision of this method as compared with that of the 1937 vacuum fusion technique.

V. HYDROGEN CONTENTS OF MISCELLANEOUS FERROUS MATERIALS

The observation that a sample of quenched 18 chromium-8 nickel steel contained a high content of hydrogen and retained it tenaciously during storage for 11 days called attention to the reports of other investigators [4, 7, 17, 19, 22] on the effect of alloying elements on the solubility and rate of diffusion of hydrogen. Accordingly, determinations before and after heating in hydrogen were made on some plain and alloy steels. The results are shown in table 2.

The material for samples 1 to 8 was in the form of hot-rolled rods approximately 1 inch in diameter. Materials 9 to 11 were forgings, and materials 12 and 13 were cores from billets which had been milled to prepare two of the Bureau's Standard Samples. Materials 14 and 15 were 1-inch rods of similar composition but different heat treatment.

The results from the first eight samples of the hot-rolled rods failed to show any correlation of composition with the hydrogen content. After heating in hydrogen at $1,100^{\circ}\text{C}$, the quenched specimens contained about the same amounts of hydrogen, usually a little less than

the remelted electrolytic-iron specimens shown in figure 3. The variations in these results and the occasional low values are probably the result of variations in the temperature of the hydrogen treatment and in the speed of quenching rather than the effect of any differences in composition.

TABLE 2.—Hydrogen contents of some plain and alloy steels before and after annealing in hydrogen at 1,100° C

Sample No.	Description	Composition						Hydrogen—	
		C	Mn	Si	Ni	Mo	Cr	In original material	After H ₂ -anneal and quench
		%	%	%	%	%	%	%	%
1	Ingot iron	0.016	0.024	0.001				0.00001	0.00046
2	Plain carbon steel	.03	.31	.002				.00002	.00031
3	do	.12	.72	.02				.00004	.00041
4	do	.17	.65	.09				.00002	.00037
5	do	.20	.45	.03				.00004	.00039
6	do	.22	.45	.14				.00002	.00035
7	do	.42	1.15	.26				.00001	.00036
8	do	.43	.47	.20				.00002	.00033
9	Alloy steel	.34	.60	.26	3.5		0.09	.00003	.00042
10	do	.39	.66	.29		0.5		.00002	.00045
11	do	.36	.58	.16		.2	.82	.00003	.00040
12	do	.31	.28	.36			14	.00005	.00075
13	do	.06	.56	.76	8.4		17.6	.00038	.00071
14	do	.24	.37		9		19.6	.00001	
15	do	.24	.28		8		19.6	.00010	

The low-alloy steels, 9, 10, and 11, likewise had low hydrogen contents before treatment. After heating in hydrogen at 1,100° C, the samples contained 0.00040 to 0.00045 percent of hydrogen, similar to the values for irons and simple steels. Higher values, however, were obtained with specimens of higher chromium contents. Sample 12, with 14 percent of chromium, had a low initial content of hydrogen but retained 0.00075 percent, twice as much as the simple steels, after quenching from 1,100° C. Sample 13 likewise retained a large amount of hydrogen after heating and quenching.

The high content of sample 13 (0.00038 percent) apparently reflects a lack of hot work in the previous history of this material. Two additional specimens of the 18–8 type, which had been hot-rolled to 1-inch rod, were available. Steel 15, without any thermal treatment except that incidental to the hot rolling, contained 0.00010 percent of hydrogen. This value resembles the hydrogen contents of the hot-rolled rods of simple steels rather than that of steel 13. Sample 14, which had been annealed for 8 hours at 735° C, subsequent to hot working, contained 0.00001 percent of hydrogen. Newell [22] found that ingots and castings frequently have high hydrogen contents and that hot working lowers these values.

The data in table 2 therefore indicate that the hydrogen contents of hot-rolled steels usually are low and that the hydrogen contents of samples of 18–8 steel decrease with increasing amounts of hot work or annealing. The amount of hydrogen retained after heating in hydrogen at 1,100° C and quenching was not appreciably affected by variations in composition of the simple and low-alloy steels listed in table 2. The only effect of composition was that the steels with 14 and 18 percent of chromium retained approximately twice as much hydrogen as the others.

VI. CONCLUSIONS

1. The vacuum fusion method yields accurate results in the analysis of materials, like cathode iron, which contain hydrogen in a stable form and in considerable amounts. With pressuremetric analysis of the gases, the method is not so satisfactory for the determination of the small amounts of hydrogen which are present in ordinary commercial steels, because of the difficulty of determining these small amounts of hydrogen in the presence of large amounts of oxygen and nitrogen. Unsatisfactory results are obtained in the analysis of samples which contain unstable hydrogen from electrolysis or from heating in hydrogen, because of loss of hydrogen during the extended outgassing that is necessary to bring the blank correction to satisfactorily low and constant values.

2. The method of warm extraction at 800° C yields satisfactory results for a variety of steels of high and low hydrogen contents. Two advantages of this method are (1) Speed of operation, which improves the determination of fugitive hydrogen contents, and (2) evolution of hydrogen-rich gases from the specimen regardless of its contents of oxygen and nitrogen, which simplifies the determination of small amounts of hydrogen.

3. The fugitive nature of hydrogen introduced by cathodic charging or by heating in hydrogen at elevated temperatures necessitates immediate analysis. Such materials lose as much as 90 percent of their hydrogen during a few days' storage at room temperature. The high hydrogen contents of electrodeposited iron are more stable, but even this material loses hydrogen when the storage time is measured in months. High hydrogen contents produced by electrodeposition of hydrogen on the surface of solid metal are much more fugitive than similar contents produced by codeposition of iron with the hydrogen.

4. Hydrogen contents of ordinary ferrous materials after extended storage at room temperature, particularly if they were hot-worked in fabrication, usually approximate the solubility of hydrogen in iron at room temperature and therefore are stable.

5. Analyses of long rods of seven mild steels and an ingot iron fail to reveal evidences of transverse or longitudinal segregation of the hydrogen.

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