

Conclusions.—The persistent yellow color which is sometimes formed toward the end of the reduction of arsenic acid by potassium iodide, hydrochloric acid and sodium thiosulphate is not due to the formation of sols of arsenic trisulphide, because this colloid is readily flocculated by concentrated hydrochloric acid, which is here present. The conclusion seems obvious that arsenic triiodide is formed in a colloidal state, in presence of an excess of potassium iodide.

With conditions maintained as in the official method, no interfering color is formed during the reduction, unless the specified quantity of 1 gm. of potassium iodide is exceeded. Variation in acidity within reasonable limits has no undesirable effects, so far as development of color is concerned, but it is necessary to exercise care in weighing the iodide to be used in the reduction. No doubt a lack of appreciation of this requirement has been responsible for the apparently erratic results often observed by analysts, who have thought that they were following the same method in all cases.

The older method, as herein outlined, seems preferable to the distillation method of Roark and McDonnell, which is now official. If the analyst will exercise some care in the addition of potassium iodide he will experience no difficulty in obtaining accurate and reliable results.

THE DIFFUSION OF HYDROGEN IN IRON.

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It is quite well known among metallurgists that metals may dissolve various gases, sometimes in fairly high concentrations. This is especially true for metals in the molten state and gases so dissolved are partly expelled when the metals crystallize during solidification, this action resulting in troublesome "blow holes," which are merely gas pockets occurring through the mass of solid metal.

It seems practically certain that, within ordinary temperature ranges, most gases may enter into metallic solution only if the gas be in the atomic state. But if a gas is liberated from a compound, in direct contact with a clean metal surface and by reaction of the compound with the latter, solution is relatively easy because the gas is then in the nascent state.

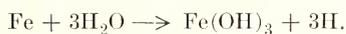
This action is especially important in connection with the operation of cleaning sheets of iron or mild steel to prepare them for coating with tin, zinc or enamel. During the process of rolling the metal into sheet it becomes coated with iron oxide which, if not first removed, will effectively prevent the second metal alloying with the iron surface, during the tinning or "galvanizing" process. In order to remove this oxide coating the sheets are "pickled" in hydrochloric or sulphuric acid. The concentration, temperature and duration of application of the acid are so chosen as to effect complete removal of scale, with a minimum of attack upon the metal underneath. But under any circumstances there

is some solution of free iron, with the formation of ferrous sulphate (or ferrous chloride) and hydrogen.

When hydrogen is evolved by a reaction between a metal and an acid, much of it ordinarily escapes as bubbles of gas. This is due to immediate combination of the atoms of hydrogen to form diatomic molecules of ordinary gaseous hydrogen. But if the nascent hydrogen is in contact with any other substance with which it can react (an oxidizing agent) it is not so evolved. Similarly, if any solvent for atomic hydrogen were present at the moment of liberation, thus preventing intercombination of the separate atoms, such solution could occur at the surface of attack by the acid from which the hydrogen is liberated.

This would appear to be true in the case of iron and acids. At ordinary temperatures gaseous (molecular) hydrogen will not dissolve in iron. But during the pickling of iron or steel sheets considerable quantities of hydrogen are absorbed, this element diffusing into, and ultimately through the sheets. If such dissolved hydrogen is not removed by a subsequent annealing the metal will be found to have become quite brittle. Frequently also small blisters appear in the sheet during the coating process.

Embrittlement of steel by hydrogen sometimes occurs in other cases. For example, steam boilers occasionally become brittle and yield to internal steam pressure. This is thought to be due to absorption of hydrogen from alkaline water, due to such a reaction as the following:



Most of this hydrogen escapes as the molecular gas but some of it dissolves in the ferrite, or iron grains, of the steel.

All metals in the normal condition possess a crystalline structure. Regular crystal outlines are not always observed but in such cases the mass of the metal is composed of irregularly formed grains, whose internal structure is certainly crystalline in character. When a section of a low-carbon steel is polished and etched with a dilute acid, microscopic examination reveals a structure like that of figure 1. In this photomicro-

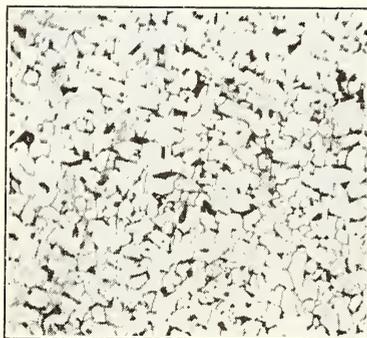


Fig. 1—Photomicrograph of a low-carbon steel, 100x.
(Reduced one-third.)

graph the bright portions are grains of ferrite, or carbonless iron. The small dark grains are of pearlite, the eutectoid of iron and iron carbide, while the network of fine, dark lines consists of grooves produced by the action of the etchant upon the grain boundaries, which are of supposedly amorphous metal.

The mechanism of solution and diffusion of hydrogen in iron has not been thoroughly understood, although considerable attention has been given to the problem. A partial bibliography of the subject of hydrogen solution and of embrittlement of steel has been given by Edwards.¹ This indicates that the first recorded observation of the general phenomenon was made by Cailletet² and that many others have studied various phases of the question since that time.

Edwards studied the influence of variation in time and temperature, and in concentration of hydrochloric and sulphuric acids, upon the rate of solution and diffusion of hydrogen. His method consisted in allowing the acid to act upon one side of a clean sheet of hot-rolled mild steel, the hydrogen which diffused through to the other side being collected and measured. He found that at 18° C. the rate of diffusion increased rapidly as the concentration of sulphuric acid was increased from 5 to 15 per cent, but slowly for further increase in concentration. For acid of a given concentration (tenth equivalent normal) the rate of solution and diffusion was practically inversely proportional to the temperature.

In order to account for the formation of blisters in pickled sheet, before or after annealing, Edwards advanced the following theory:

Hydrogen dissolves in the steel in the atomic state and diffuses in this form. When the atoms reach any surface they unite to form diatomic—ordinary gaseous—hydrogen. If the surface so reached is the exterior surface of the sheet, the gas simply escapes. But if this surface is at some discontinuity of the metal, however small this may be, gas pressure is generated and a blister is developed, either at once or during the heating for annealing or coating. That such pressures may become very large was shown by Cailletet,² who proved that diffusion through the metal may take place against an opposing pressure as high as fourteen atmospheres.

Discontinuities which might serve in this way may be present at the numerous non-metallic inclusions of microscopic dimensions, always found in iron and steel, as well as at larger flaws in the form of blow holes and at accidentally enclosed particles of iron oxide.

It has been supposed by Andrew³ and others that hydrogen diffuses largely or entirely through amorphous grain boundaries and that its solubility in the crystalline body of the grains is very small. This assumption would account, in a way, for the intercrystalline brittleness usually noticed in pickled steel. If this were true a fine grained metal should permit greater freedom to the passage of gas than a coarse grained one, since in the former case there is a greater relative quantity of the amorphous phase. Edwards made a single test of this theory by observing the rate of diffusion through two sheets, one of which was

¹ J. Iron and Steel Inst., 110, 9-44 (1924).

² Comp. rend., 66, 847 (1863).

³ Trans. Faraday Soc., 9, part 3 (1914).

made from a single large grain of iron, the other having had the grain refined by thermal treatment. He observed no difference in the rate of diffusion in the two cases.

Experimental. Sheets of 26-gauge ingot iron (0.019-inch in thickness), furnished by the American Rolling Mills Co., were used in the experiments. Strips about one inch wide and two inches long were cut from this and the ends were bent up to assist in holding during the polishing. The lower sides of the strips were then polished and etched in the usual way to prepare them for microscopic examination, after which glass cells, made by cutting from the tops of test tubes, were cemented to the bright upper surfaces. DeKhotinsky medium cement was used for this purpose. The entire assembly is shown in figure 2.

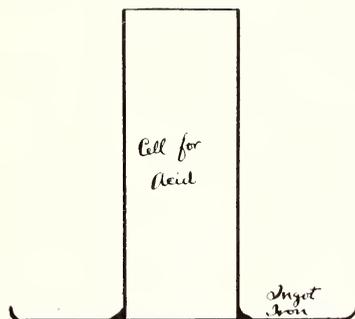


Fig. 2.—Acid cell and specimen for diffusion experiments.

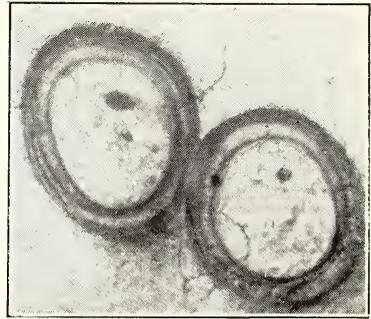
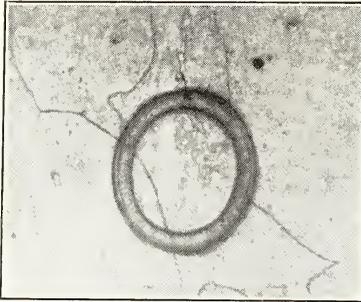
This is somewhat similar to the assembly used by Edwards, except that his experiments were concerned with the effort to measure the diffused hydrogen. Edwards clamped the glass cell to the upper surface of his sheet steel, a wide tube filled with water being fastened to the lower side. In this way he was able to collect the hydrogen which passed through the metal.

The polished and etched lower surfaces of the metal used in the present investigation were lightly smeared with a greasy material. In this way it should be possible to observe, by means of the microscope, any localized liberation of hydrogen which had passed through the iron, microscopic bubbles being formed. Large bubbles were neither expected nor desired. The formation of macroscopic bubbles would make microscopic examination difficult or impossible, at any magnification sufficiently high to reveal the grain structure of the iron, and a substance having a low surface tension was sought, in order that only small bubbles might be retained. At the beginning a number of materials were tried for this purpose but a neutral petrolatum was found to serve as well as any. Approximately normal sulphuric acid was used in the cells and this was allowed to act without heating for several hours, the lightly greased surface being examined from time to time through the microscope.

Bubbles in the petrolatum were observed after about two hours. As the film was quite thin, these bubbles did not grow to any considerable

size but they were plainly visible under magnification. The entire surface was examined and numerous photomicrographs were made. Figures 3 and 4 illustrate typical appearances of the bubbles.

Discussion. If there is any general preference for amorphous grain boundaries, on the part of diffusing dissolved hydrogen, one might expect to observe trains of bubbles following the network of grain boundaries appearing in the sections. No such manifestation was observed. In many cases grain boundaries ran through the areas covered by bub-



Figs. 3 and 4—Gas bubbles from hydrogen diffused through ingot iron. 350x.
(Reduced one-third.)

bles; but too many other bubbles appeared within the meshes of the network to warrant any assumption of this particular mode of travel by diffusing hydrogen.

On the contrary, a large majority of the bubbles were found to be located in such a manner as to cover non-metallic inclusions—microscopic particles of manganese sulphide or of slag. In figure 4, which illustrates the appearance of most of the bubbles, these inclusions are seen as the dark spots appearing within (or at the edge of) bubbles. There is no inclusion of appreciable size appearing under the bubble of figure 3, as was the case with a few others not photographed. But even here it is possible that an inclusion is located barely beneath the exposed surface—so close to this surface that compressed gas could readily burst its way through. The grain structure under this bubble suggests this as the correct explanation. Of course this cannot be stated as a positive conclusion but the large preponderance of bubbles appearing over inclusions, as well as the observed absence of trains of bubbles following the network of grain boundaries, seems to justify the conclusion that the explanation of Edwards is correct: that hydrogen follows no preferential path in its travel through iron or steel, but that at the surfaces bounding inclusions atomic hydrogen collects and forms molecular gas under high pressure, this being responsible for the formation of blisters. It is assumed, in the interpretation of the present experiments, that the major portion of diffusing gas is so uniformly distributed over the surfaces of grain sections, at the surface of liberation, that it finds its way through the thin grease coating without the formation of observable bubbles.