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The Diffusion of Hydrogen Through Carbonyl Iron at Temperatures from 800° to 1100° Centigrade

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(Received July 24, 1937)

The diffusion of hydrogen through hydrogen-purified carbonyl iron shows breaks in the $\log(\text{rate})$ vs. $1/T$ curve at 834, 909 (body-centered→face-centered phase change), 945, 1009, 1056, 1082 and 1103 deg. centigrade. These are average values for three samples of "Mehl" iron. The $\log(\text{rate})$ vs. $1/T$ curves at these temperatures are composed of arcs, the above points being ends of these arcs. These points fall on a line whose slope is 4085 deg. Kelvin. Thus b in the expression $\exp(-b/RT)$ is given as 18,680

cal./g atom for these points. The above temperatures belonging to the ends of the arcs can be fitted to a Balmer type formula, i.e., $T(^{\circ}\text{K}) = C(1/3^2 - 1/n^2)$, where $n = 6, 7, 8, \dots$, and $C = 13,430 \pm 30$ for the breaks starting with $n = 7$, while $C = 13,301$ for the break with $n = 6$. This difference is presumably caused by the $n = 6$ break being in the body-centered phase, while all breaks starting with $n = 7$ are in the face-centered phase.

DURING the past year we have developed the experimental technique previously reported by one of us¹ in order to study the diffusion of gases through metals at high temperatures. These studies, at the present time, are concerned with the diffusion of hydrogen through iron and nickel, especially the former element. We have investigated the diffusion of hydrogen through iron from 60° to 1100° centigrade,² in steps of 5 to 10 degrees, and it will be obvious that with precision technique, the state of affairs represented by the previous conclusions derived from data on iron is far from the truth. When only a few points are taken on the isobars, most of the important characteristics are apt to be attributed to experimental error.

Borelius and Lindbloom,³ Ryder,⁴ and more recently, Smithells and Ransley⁵ have studied the diffusion of hydrogen through iron at temperatures ranging from 245° to 780° centigrade. The data presented by these authors is in a region in which the diffusion is fairly regular, consequently they have drawn straight lines through their $\log D$ vs. $1/T$ plots in order to determine the work function b in the expression⁶

$$D = AP^{\frac{1}{2}}T^{\frac{1}{2}} \exp(-b/RT), \quad (1)$$

¹ W. R. Ham, *Am. Soc. Metals*, **25**, 536-564 (1937).

² Mr. W. L. Rast will shortly publish his data on the lower temperature runs for "Mehl" iron.

³ Borelius and Lindbloom, *Ann. d. Physik* **82**, 201 (1927).

⁴ Ryder, *Elec. J.* **17**, 161 (1920).

⁵ Smithells and Ransley, *Proc. Roy. Soc.* **A150**, 172 (1935).

⁶ Richardson, Nicol and Parnell, *Phil. Mag.* **8**, 1-29 (1904).

where D is the rate of diffusion measured in grams of hydrogen diffusing through unit area per mm thickness at the temperature T , and A is a constant of proportionality. Eq. (1) assumes that the pressure P is exerted by the gas on one side of the diffusing material and a vacuum is maintained next to the outgoing face.

Smithells and Ransley⁵ have shown quite clearly that the diffusion of hydrogen through iron takes place *through* the lattice. Their experiment consisted in showing that the diffusion through iron gave the same rate for a single crystal as for a polycrystalline sheet. The familiar $P^{\frac{1}{2}}$ relationship for pure metals, as given by Eq. (1), suggests that the hydrogen goes through the lattice in the atomic form.^{6, 7} Fowler⁸ has considered the solution of gases in metals by assuming the gas to be present in the metal as protons and electrons.

We have found that every important structural, or phase change, in the sample under investigation can be recognized by the diffusion rates. Thus the Curie region in pure iron and nickel can be recognized. Since this region is not distinguished by a change in crystal structure, but is to be accounted for by changes in the electronic structure of the iron lattice,⁹ we must conclude that the rate of diffusion of hydrogen through iron and nickel is intimately connected

⁷ Donnan and Shaw, *J. Soc. Chem. Eng.* **29**, 987 (1910).

⁸ R. H. Fowler and C. J. Smithells, *Proc. Roy. Soc.* **A160**, 37 (1937).

⁹ J. C. Slater, *Phys. Rev.* **49**, 537 (1936); *ibid.* **49**, 931 (1936).

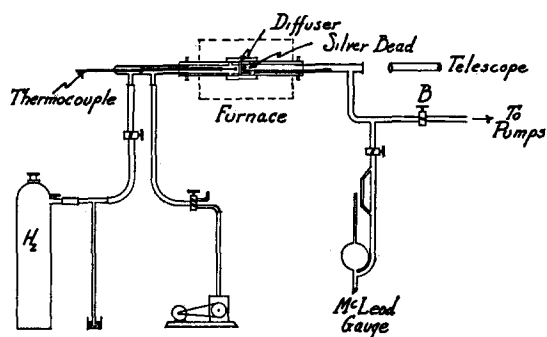


FIG. 1. Apparatus for "steady-state" and trapping methods.

to the electric fields surrounding the lattice points.

A change in crystal structure can be recognized very clearly. The body-centered to face-centered phase change in pure iron is easily recognized, in fact, the rate of diffusion is halved in passing from the body-centered to the face-centered form. In all probability, the change in rate of diffusion between these two structures is due to the interaction of the hydrogen ion, or atom, with the field. Although the detection of these electronic and structural changes does not prove definitely which of the two forms, atomic or ionic, exists in the diffusion of gases through metals, we feel that to account for the magnitude of the change in rates we must assume the ionic form for hydrogen as it passes from point to point of the lattice. The hydrogenic electrons will presumably become a part of the free electrons of the metal, as suggested by Fowler.⁸

In addition to the above arguments for the ionic form, we have found a new temperature effect for the diffusion of hydrogen through iron which is definitely outside the limit of our experimental error. When the high temperature data is plotted in the form of $\log(\text{rate})$ versus $1/T$, we find that the curve is composed of arcs, the end points of the arcs being characteristic of hydrogen through iron. The temperatures of the end points of these arcs can be fitted to a Balmer type formula, where the constant "term-value" belongs to the number 3. We have followed this series up to the temperature 1103° and although there is indication that further breaks lie above this temperature, we cannot resolve the breaks sufficiently to fix, experimentally, the running coordinate n in the formula.

EXPERIMENTAL PROCEDURE

A detailed description of the apparatus is to be found elsewhere,¹ but we will give a short description of the apparatus and a detailed description of the experimental procedure used here to establish the validity of the results. Fig. 1 is a schematic drawing of the necessary equipment needed for the steady-state, and trapping, methods.

The essence of the "steady-state" method lies in having the stopcock B barely open to the pumps. A small back pressure (10 to 60 microns, i.e., 10^{-4} cm Hg) is obtained which can be read on a McLeod gauge. When the opening through the stopcock B is very small a larger pressure is obtained. This we designate as "increasing the sensitivity." The sensitivity will be given as the ratio of the pressure when the cock B is barely open, to the rate (as read on the gauge) when the cock is entirely open to the pumps. It is necessary that the McLeod gauge be as accurately calibrated as possible and then recorrected by timing the build-up in pressure when only a small amount of gas is being trapped by diffusion through the sample.

That the steady-state method gives consistent results with the trapping methods is shown in Fig. 2. Here we have plotted the log of the rate as determined by the trapping method against the log of the steady state rate. This graph is important because of the fact that previous investigators have used the trapping method. The diffusion rate of hydrogen through iron and nickel at high temperatures is relatively high

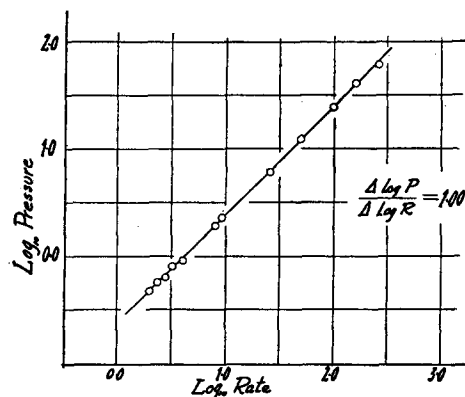


FIG. 2. Log (steady-state pressure) versus log (trapping rate).

unless reduced pressures are used on the ingoing side of the diffuser. Reducing the pressure is valid for a small number of points, but since we take readings every 5 degrees at these temperatures we find that more accurate results can be obtained by keeping the ingoing pressure at atmospheric conditions and then correcting the rates by the $P^{\frac{1}{2}}$ law to 760 mm Hg. Fig. 2 shows that the two rates are directly proportional to one another.

Figure 3 is a detailed sketch of the diffusers used and the type of assembly. Diffuser (1) was made by welding with atomic hydrogen the "Mehl" iron¹⁰ disk to a nickel tube. After machining to the desired thickness this outside nickel tube was atomic hydrogen welded to smaller nickel tubes. The wall thickness of these nickel tubes was 3/16 inch. Water coolers were placed at the ends for deKhotinsky joints to the vacuum system and hydrogen inlet. This type of diffuser was abandoned after one trial because of nickel contamination in the welding. The baffle plates of pure iron were to protect the diffuser when the ends were welded to the sample holder. Diffuser (2) has been the most successful of the types made to date. The iron disk was atomic hydrogen welded to two pieces of Armco iron tubing. This tubing had been previously baked for 50 hours at 1100°C in hydrogen for the purpose of removing most of the carbon present in this low carbon iron. The baffle plates were then inserted and the inside unit gold (or copper) welded to the outside nickel tube. All of these operations were carried out with a hydrogen atmosphere next to the diffusing disk. The ends were then atomic hydrogen welded to the whole central unit after the disk had been machined to the desired thickness (usually 60 to 80 mils for high temperature diffusion studies).

The furnace was thermostated by means of a photoelectric cell circuit. The controlling thermocouple was placed next to the heating coils in the furnace. The heating coils were separated from the diffusing tube by about 3/8 inch of porcelain. This position of the controlling couple gave exceptionally good results because the

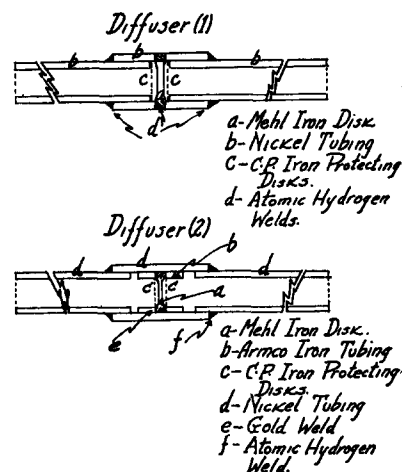


FIG. 3. Diffuser assembly for Mehl iron samples.

proximity of the couple to the heating coils enabled the circuit to completely control the temperature at the center of the heating coils. Since these coils were so near the diffusing tube, the temperature of the diffusing disk remained constant over any length of time desired.

The temperatures of the disk were read by means of a chromel-alumel thermocouple, size 18 wire, inserted in through the hydrogen end and placed 1 mm distant from the disk. This wire had been standardized by the National Bureau of Standards.¹¹ In order to make sure that the couples were not drifting with time we would check them before and after a run by means of the melting point of 99.98 percent purity silver as follows. A small bead of this silver was placed on an iron holder. This holder was connected to a piece of nickel by means of a lightweight Nichrome wire. The nickel piece protruded from the nickel tube of the diffuser to such a distance that it could be manipulated by magnets. The holder was then slid up against the disk and the melting point ascertained by means of visual observation through the telescope shown in Fig. 1. The thermocouples are thus standardized while in the position they occupied during the run.

The temperatures recorded by the inside couple were read by means of a Leeds and Northrup type K potentiometer using a galvanometer with a current sensitivity of 2.72×10^{-6} amp./mm

¹⁰ We must express our thanks to Dr. F. R. Mehl of the Carnegie Institute of Technology for furnishing us with a supply of his hydrogen purified carbonyl iron. This carbonyl iron was purified by baking at 1100°C in an atmosphere of purified hydrogen. For a description of this iron see reference 13.

¹¹ We wish to thank Mr. Roesser of the National Bureau of Standards for furnishing us this thermocouple wire and standard silver beads.

deflection. The galvanometer resistance was 4.4 ohm. The thermostat held the temperature constant to less than 1/4 mm deflection on the potentiometer galvanometer. This means that the temperature was constant to within ± 0.07 degrees at temperatures up to 1125°C.

Leak tests were run by substituting helium for hydrogen. The leak test in all of these runs amounts to only about 2 percent of the recorded rate. The readings were corrected to take account of this leak rate. At the beginning of a run the diffuser was taken to a temperature about 25 degrees above the highest recorded temperature used for a rate reading. The diffuser was held at this temperature (usually 1125 deg. C.) with the pumps and hydrogen on for about an hour. The rate would then be lowered in small steps of about 5 to 10 degrees to about 875°C. The rate would then be read as the temperature was raised back to the starting temperature. At these temperatures a steady state is reached in about 10 minutes. In all cases, readings of the pressure would be taken until a duplicate reading was obtained. Considerable trouble was experienced in obtaining complete runs of this kind because of the nichrome winding of the furnace failing at these high temperatures. Several complete runs were obtained in addition to much data over limited regions.

All of the results up to 1000 deg. C reported here have been checked by different observers and two other sets of apparatus at this laboratory.

EXPERIMENTAL RESULTS

Figure 4 is a direct plot of the diffusion rate of hydrogen through Mehl carbonyl iron against the temperature in millivolts (uncorrected).¹² The corrected temperatures are clearly indicated at the breaks. It is unfortunate that a low sensitivity was used in Fig. 4, otherwise the breaks at 955° and 1010° would show to better advantage when plotted to this small scale. The higher breaks are clearly defined at this sensitivity. It is significant

¹² All of the data shown in this paper was plotted after the readings were taken. No objection should be raised to plotting the temperature as millivolts in Figs. 4, 5, and 6 because the features we wish to point out in these curves are the breaks. The National Bureau of Standards thermocouple wire used here was selected because of its linear relationship between e.m.f. and temperature. The corrected temperatures of the breaks are clearly indicated.

that the $\gamma \rightarrow \alpha$ phase change, which normally occurs at 910°C for this type of iron,¹³ has been supercooled to 856°C when the sample is brought in these small steps from 1125°C. A repeat run with a technique to be discussed in a later paper on the rates of transformation of this phase change, shows the $\gamma \rightleftharpoons \alpha$ transformation to occur at 890°.

Figure 5 shows the breaks at 951° and 1014° for another sample. This run was made at a higher sensitivity than Fig. 4 and the lower breaks are clearly defined. Fig. 5 also illustrates the type of diffusion break found at the crystal structure change.

Figure 6 shows the rate of diffusion of hydrogen through a sample contaminated with nickel. This diffuser was of the first type described. Each of the "break" points has been lowered in a regular manner and also decreased in intensity. We will shortly publish some data on the diffusion of hydrogen through nickel, and we can anticipate this publication by saying that such a series of breaks as is found here in pure iron has not been found in nickel.

Figure 7 shows the appearance of these breaks when the log of the steady state rate is plotted against $1/T$, where T is in degrees Kelvin. The deviation of the curved lines from the dashed straight line are definitely outside the range of experimental error. Furthermore, if an error in

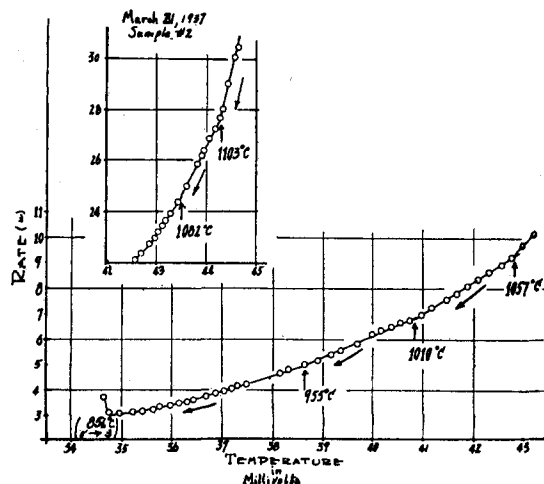


FIG. 4. Diffusion rate of hydrogen through Mehl iron versus temperature in millivolts (uncorrected).

¹³ Wells, Ackley and Mehl, Trans. Am. Soc. Metals 24, 46 (1936).

the apparatus caused the deviations, it would certainly be expected that the deviations would be erratic. This latter point bears more weight when it is considered that the points shown on the graphs represent only one out of three or four points. This is necessary because of the difficulty of drawing small graphs so that they may be legible. The straight line which can be drawn through each of the "breaks" in Fig. 7 has a slope of 4085 abs. deg., hence b in the expression

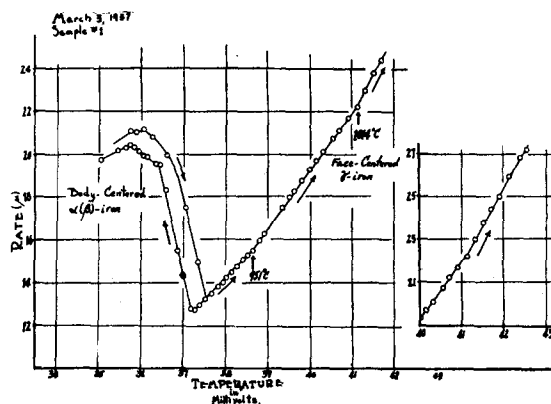


FIG. 5. Diffusion rate of hydrogen through Mehl iron versus temperature in millivolts (uncorrected).

$\exp(-b/RT)$ is 18,860 cal./g atom for these points.

The data obtained for the temperature of the body-centered to face-centered phase change are not to be trusted in view of the excellent determination of this point recently made by Wells, Ackley and Mehl.¹³ The chances for slight contaminations at high temperatures are too great to record our temperatures of the $\alpha \rightleftharpoons \gamma$ transformation as belonging to pure iron. Slight contaminations will lower this point in a surprising manner which can be accounted for by use of the Van't Hoff freezing point lowering formula. Austin¹⁴ gives $\Delta H = -218$ cal./g atom as the heat effect at the transition, $T = 1183^\circ\text{K}$, whence 1.27×10^4 is the lowering of the phase change temperature in the infinitely dilute solution, per mol of impurity in one gram atom of iron, providing the impurity is insoluble in the body-centered phase. While these small amounts of contamination make our results inaccurate for the determination of this temperature, never-

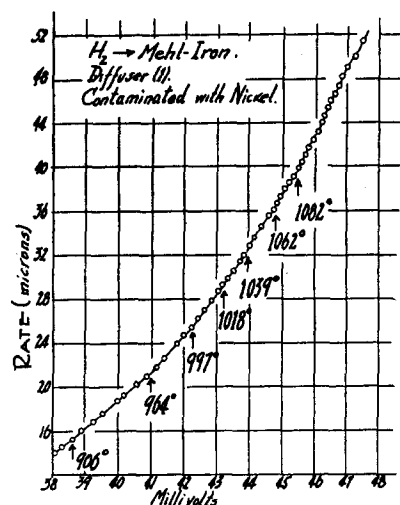


FIG. 6. Diffusion of hydrogen through Mehl iron contaminated with nickel.

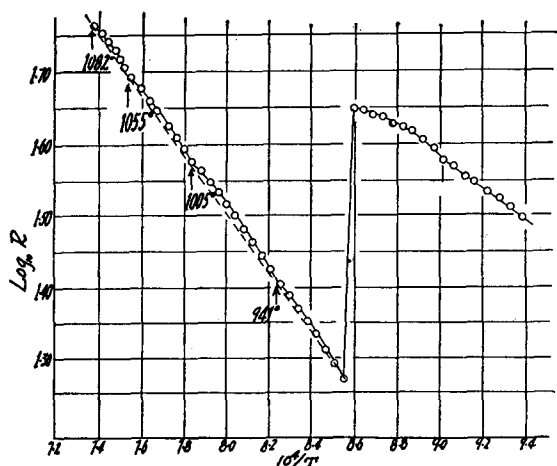
theless we feel that small amounts of contaminant do not effect appreciably the location of the breaks given above excluding, of course, the body-centered face-centered transformation. Table I bears out this latter conclusion. Here we list the temperatures obtained for these breaks from three different samples. The temperatures of the breaks up to, and including 1014 have been obtained many times on samples which were not taken to higher temperatures. The sample which shows the breaks lowered appreciable amounts (Fig. 6) is obviously heavily contaminated with nickel.

DISCUSSION OF RESULTS

Ham¹ previously noted the existence of the 835 and 945 degree breaks, both in iron obtained from Yensen, of the Westinghouse Laboratories, and in Mehl iron. He also suspected the existence of the break at 1010 degree cent., but he did not take his samples to a high enough degassing temperature to be sure of this latter break. This would indicate that the existence of this series is not alone limited to Mehl iron, in fact we may say, that this series should be characteristic of all pure carbonyl iron which has been purified so that it approaches closely the purity of pure iron.

At this time we wish to recapitulate the following pertinent points: (1) That our temperature control is good to within ± 0.07 degrees for all temperatures recorded here, (2) That the previ-

¹⁴ J. B. Austin, Eng. Ind. Chem. 24, 1225 (1932).

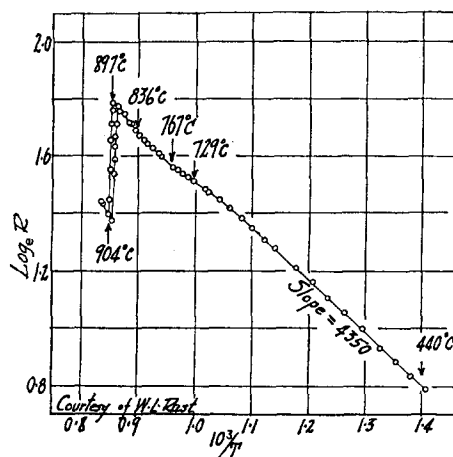
FIG. 7. Log R vs. $1/T$ for hydrogen through Mehl iron.

ously standardized inside thermocouple was rechecked at the melting point of 99.98 percent purity silver while in the position it occupied during the runs, (3) That the precision of the pressure readings is limited only by the accuracy of reading the McLeod gauge (this error on Fig. 7 amounts to less than half the width of the circles drawn there), (4) That the breaks up to, and including, the temperature 1012° were previously shown in graphs by Ham,¹ and that these breaks up to 1012° have been checked by different observers on two other sets of apparatus during the past year, (5) That equilibrium was reached in all these readings as shown by the fact that the same temperature was held until a duplicate reading was obtained for the diffusion rate before moving on to the next temperature, (6) That Figs. 4 and 5 represent the general characteristics of these breaks and that the abruptness of the change in slope can be controlled somewhat by the sensitivity of the apparatus (see "Experimental Procedure"), and (7) that we have obtained limited runs throughout this region which is in agreement with Figs. 4, 5, and 7, but which are not shown because of lack of space.

We early sought for a series which would express these experimentally determined points. These breaks were found to fit a Balmer type

TABLE I. *Temperature of breaks in diffusion curves, hydrogen through iron.*

Sample No. 1	835	955	1010	1057	1082	1103
Sample No. 2	833	941	1005	1055	1082	—
Sample No. 3	836	951	1014	—	—	—

FIG. 8. Log R vs. $1/T$ for carbonyl iron for temperature range 440° to 925°C .

formula. We find it necessary to give the number 3 to the fixed "term-value," consequently n , the running coordinate, will take the values 6, 7, 8, \dots . This series, with its constant, is as follows:

$$T(^{\circ}\text{K}) = (13,430 \pm 30)(1/3^2 - 1/n^2). \quad (2)$$

Table II gives the temperatures, the values of n , and the constant computed from the experimental data. The average value with its deviation is $13,430 \pm 30$ for the breaks starting with $n = 7$. The first value was not averaged with the following because we feel that it should be different from the others for the obvious reason that the first break lies in the body-centered phase, while all the others lie in the face-centered. If this series is connected in any way with the interplay of forces between the hydrogen ion and the electric fields surrounding the iron lattice, then we would expect the forces to be different for the iron in the body-centered form and in the face-centered form.

TABLE II. *Determination of constants in series for experimental breaks.*

TEMP. ($^{\circ}\text{K}$)	n	CONSTANT	DEVIATIONS
1108	6	13301	—
1222	7	13472	+42
1283	8	13434	+4
1329	9	13455	+25
1355	10	13403	-27
1376	11	13385	-45

Average Constant = 13430 ± 30

That the diffusion of hydrogen through iron does not follow the simple relation expressed by Eq. (1), except over limited regions, is shown by Fig. 8. Here we show the log (rate) *vs.* $1/T$ for a sample of Mehl iron in the range from 925° to 300°C. Mr. W. L. Rast will shortly publish his data on these low temperature runs and discuss them in detail, in addition to discussing the anomalous behavior of hydrogen through iron below 300°. In the meantime we are indebted to Mr. Rast for allowing us to reproduce Fig. 8.

This graph also makes it clear why previous investigators only reported the range of diffusion from about 750 to 300°C. This region does correspond, to a first approximation, to Eq. (1), and if only a few points were taken it is clear that one would think that the log (rate) *vs.* $1/T$ curves should be linear. The general features of Fig. 8 have been consistently obtained for pure iron over a period of several years. These observations have been made by different observers and three different sets of apparatus.

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The Crystal Structure of Potassium Metaborate, $K_3(B_3O_6)$

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(Received August 23, 1937)

In order to find the configuration of the metaborate group the crystal structure of potassium metaborate was determined. The crystals are rhombohedral $a_r = 7.76\text{\AA}$, $\alpha = 110^\circ 36'$ with six molecules KBO_2 . The density is 2.348. The space group is $R\bar{3}c(D_{3d}^6)$. All atoms are lying on twofold axes at positions: $\pm(u, \frac{1}{2}-u, \frac{1}{2})\cdot$. The parameters were determined by means of two-dimensional Fourier analyses:

$$\begin{array}{ll} K & u = 0.689 \pm 0.003, \quad B \quad u = 0.361 \pm 0.006, \\ O_I & 0.465 \pm 0.006, \quad O_{II} \quad 0.146 \pm 0.006. \end{array}$$

The metaborate radical is $(B_3O_6)^{-3}$, a ring of three BO_3 triangles, rather than the endless chain of BO_3 triangles found in CaB_2O_4 . The BO_3 groups are slightly distorted, the B-O distances being 1.33Å, 1.38Å and 1.38Å, the O-O distances 2.30Å, 2.38Å and 2.38Å. The nine particles of the radical lie in one plane. Potassium is surrounded by seven oxygen atoms at a distance 2.82Å.

A FEW years ago we investigated the crystal structure of calcium metaborate, $Ca(BO_2)_2$,¹ and found that it contained the metaborate groups as endless chains built up of BO_3 triangles. While our studies of the borates have convinced us of the nonexistence of radicals $(BO_2)^-$, we considered it likely that the metaborate group in some crystals occurs in a state of finite polymerization, namely as rings of BO_3 triangles. The reported symmetry and optical properties of $NaBO_2$ and KBO_2 ,² indicated that possibly such ringshaped metaborate groups might be present in these crystals, and an x-ray investigation was therefore undertaken. This article contains a discussion of the results obtained for KBO_2 .

Excellent crystals of KBO_2 were prepared by melting together K_2CO_3 and B_2O_3 in a platinum

crucible. The melt was cooled rapidly so that a crust formed on the outside. In the cavity thus produced in the interior needleshaped hexagonal crystals (up to two cm long) were found. The density was determined by the suspension method (using methylene iodide and toluol) to 2.348 ± 0.005 . The crystals are hygroscopic and were kept in minute desiccators during the x-ray exposures.

The crystals were examined by the oscillation and Laue methods. The oscillation photographs were taken with copper radiation filtered through a nickel film.

For the dimensions of the hexagonal cell we found:

$$a = 12.75 \pm 0.02\text{\AA}, \quad c = 7.33 \pm 0.04\text{\AA}.$$

However, the true unit cell is rhombohedral and has dimensions:

$$a_r = 7.76\text{\AA}, \quad \alpha = 110^\circ 36'.$$

It contains six (5.98) molecules KBO_2 .

¹ W. H. Zachariasen, Proc. Nat. Acad. **17**, 617 (1931); W. H. Zachariasen and G. E. Ziegler, Zeits. f. Krist. **83**, 354 (1932).

² S. S. Cole, S. R. Scholes, C. R. Amberg, J. Am. Ceram. Soc. **18**, 58 (1935).