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Citation: [The Journal of Chemical Physics](#) **6**, 598 (1938); doi: 10.1063/1.1750131

View online: <http://dx.doi.org/10.1063/1.1750131>

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The Diffusion of Hydrogen Through Nickel

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(Received July 20, 1938)

The diffusion of hydrogen through commercial and very pure anode nickel has been studied in a precision manner throughout the temperature interval 1100° to 150° Centigrade. It was found that the diffusion rates vary in a perfectly regular manner throughout this region, except for a discontinuity at the Curie point, namely near 360°C.

A very exact agreement with the formula $R = AT^z p^y \times \exp(-b/T)$ was found in all cases. After long heat treatment with hydrogen the value of y in the above equation for anode nickel becomes $+0.50 \pm 0.01$ with the possible exception of a region within 3° of the Curie point. All the nickel used had isotherms whose slope at the start of observations was a maximum in the Curie region and markedly greater than 0.5, but which approached 0.5 as the heat treatment, ordinarily considered as having a decarburizing effect, progressed.

The magnetic transition as shown by diffusion is abrupt, the isobars below the Curie region being quite as straight as above. There is always a sudden drop in the value of b as calculated from the simple equation $R = A \exp(-b/T)$ at the Curie point, the value changing in the purest nickel from 6600 to 5800 with rising temperature. No systematic breaks appear in the isobars at high temperatures, such as

found in pure iron, but nevertheless the value of z indicates that the diffusing hydrogen possesses appreciable energy within the lattice.

The Curie region shows marked hysteresis, and is similar to the Curie region of pure iron in this respect.

Existing theories of ferromagnetism seem to require modification, inasmuch as the Curie transition in nickel appears to take place about as abruptly as the body-centered-face-centered transition in iron. The loss of magnetism at the Curie transition is essentially an atomic phenomenon and should not be associated primarily with conditions in aggregates of atoms or atomic domains. During the transformation for a finite time, there appears to be an additional electron in the valence shell of some nickel lattice points.

A possible description of the process of the change from the ferromagnetic to the paramagnetic condition in the transition elements is that an electron is moved from the 3d shell to one of the 4 levels, followed more or less quickly by a drop of another 4-level electron back to such a 3d level as to result in the pairing of electron spins in the 3d shell.

THE diffusion of hydrogen through metals at high temperatures has been studied quite extensively during the past several years in the Pennsylvania State College laboratories. The data for iron have been published,¹ and in view of the anomalies found in the diffusion rates of hydrogen through iron, it was felt that a precision study of the diffusion of hydrogen through nickel would be justified. This study would have the double purpose of showing whether such a series of breaks in the diffusion isobars as found in iron exists in the isobars for hydrogen through nickel (incidentally this would also show whether the series was due to peculiarities of the apparatus), and also show the applicability of the steady-state method (I) to a precision study of hydrogen through nickel. Several other sets of data on the diffusion of hydrogen through nickel are available from the Pennsylvania State College laboratories,

namely Craninsky² and Ham.³ The technique has been improved from that used to obtain these two sets of data, especially the temperature control, therefore we may expect an improvement in the data for nickel. In this precision study by both the trapping and steady-state⁴ methods, we have used exactly the same apparatus, with the exception of the metal disk used for diffusion, as in I.

The diffusion rates were found to be very regular and to obey exactly the diffusion formula,⁴

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

where P is the pressure exerted by the gas on the ingoing side, T the temperature in absolute degrees, and b the so-called work function. A is a

² Craninsky, Thesis for M.S. degree, Pennsylvania State College (1932). See also Fig. 4, this article.

³ W. R. Ham, *Am. Soc. Metals*, **25**, 536-564 (1937).

⁴ Richardson, Nicol, and Parnell, *Phil. Mag.* **8**, 1-29 (1904).

¹ C. B. Post and W. R. Ham, *J. Chem. Phys.* **5**, 913 (1937), hereafter referred to as (I).

constant and D is the rate of hydrogen diffusion measured in cubic centimeters of hydrogen per square centimeter area per mm thickness at standard pressure and temperature.

The Curie point in nickel is easily recognized when the steady-state method (I) is used as a precision measure of the diffusion rates. Moreover the hydrogen diffusion rates obey the same sort of formula below the Curie point as above, consequently we can interpret the offset at the Curie point as an indication of demagnetization. The fact that the law governing the diffusion rates is the same below the Curie point as above indicates that the disappearance of magnetism is a relatively abrupt phenomenon when no field is present in the specimen and the effect is brought about entirely by temperature effects.

A marked hysteresis effect is noted at the Curie point when this transition is measured by hydrogen diffusion methods. This indicates that some of the transitions in the individual nickel atoms which are responsible for the loss of magnetism must be governed by some sort of "order-disorder" rearrangement as developed by Bragg and Williams⁵ and extended by Fowler.⁶ A possible mechanism for the demagnetization of nickel will be discussed in a later paragraph.

Isotherms were obtained above and below the Curie point. The variation of the slope of the isotherms was found to be regular above and below this point, that is, for commercial nickel the slopes varied from a value of 0.5 about 150° above the Curie point to a value of 0.56 at the Curie point (370°C) and decreased to 0.5 again about 50° below this point. A similar variation was observed with pure anode nickel except that prolonged treatment of this nickel by the diffusing hydrogen gas gradually eliminated the variation in slope from 0.5, except in a possible region within 3° of the Curie point (359.2°C). Such a variation is difficult to explain in terms of Smithells and Ransley's⁷ application of the Langmuir absorption isotherm to deviations of the pressure exponent from $+\frac{1}{2}$, but can be explained from an extension of Ham's discussion of the effect of carbon in solution in iron.

⁵ Bragg and Williams, Proc. Roy. Soc. **151A**, 540 (1935); **145A**, 699 (1934).

⁶ R. H. Fowler, Proc. Roy. Soc. **149A**, 1 (1935); **151A**, 1 (1935).

⁷ Smithells and Ransley, Proc. Roy. Soc. **150A**, 172 (1935).

EXPERIMENTAL PROCEDURE

The apparatus used in this research has been previously reported in I, and is shown here in Fig. 1. Exactly the same procedure was used in studying the diffusion rates by use of the steady-state method as reported in I.

As explained in I, the steady-state method is characterized by having a stopcock barely open to the pumps on the vacuum side of the diffusing disk. This enables a small back pressure to be built up between this stopcock and the diffusing disk, which can be conveniently read on a McLeod gauge. As shown in I, this back pressure is directly proportional to the rate as determined by the trapping method (see Fig. 2, I). We must also mention the fact that the success of this method depends to a large extent upon having a system of very fast pumps to maintain a high vacuum on the pumping side of the stopcock.

The same temperature control was used as reported in I, *viz.*, a photoelectric cell relay.

The melting point of a pure silver bead furnished by the National Bureau of Standards was noted by means of a telescope, and the thermocouples standardized without disturbing their position. The silver bead holder was manipulated by magnets outside the apparatus.

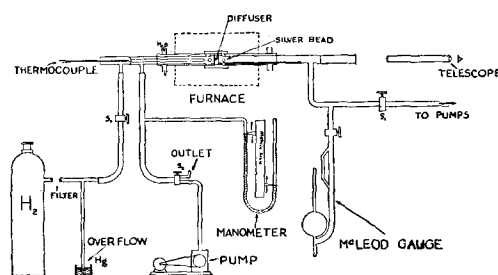


FIG. 1. Apparatus for measuring gas diffusion through metals.

Diffusers were prepared by welding the nickel diffusing disk to nickel tubes by atomic hydrogen welding as described in I.

Isotherms were obtained by operating the pump on the hydrogen inlet side of the diffuser. By manipulating the opening to this pump and the opening into the diffuser any convenient partial pressure of the hydrogen can be obtained from atmospheric down to 0.5 cm Hg. The logarithm of the rate was plotted against the log

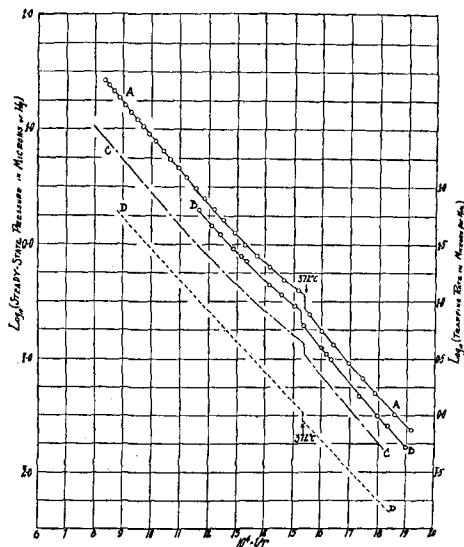


FIG. 2. Diffusion of hydrogen through commercial nickel. Sample XIII. 53 mil. AA, \log_{10} (steady-state rate) vs. $1/T$; BB, \log_{10} (trapping rate) vs. $1/T$; CC, \log_{10} (steady-state rate) $-\frac{1}{2} \log_{10} T + 1$ vs. $1/T$; DD, \log_{10} (steady-state rate) $-\frac{1}{2} \log_{10} T - \gamma \log_{10} P$ (in mm) $+1$ vs. $1/T$.

of the pressure and the slope taken to determine the value which we designate as the "slope of the isotherm."

Trapping methods were also used to establish the value of the diffusion rate in cubic centimeters of hydrogen at standard pressure and temperature diffusing through the disk per square centimeter area per millimeter thickness. These trapping rates also served to establish the proportionality factor between these rates and the rates as determined by the steady-state readings.

EXPERIMENTAL RESULTS

Figures 2 and 3 show the diffusion rates of hydrogen through commercial nickel plotted as

$$\log_{10} (\text{steady-state rate}) \text{ vs. } 1/T, \quad (2)$$

$$\log_{10} (\text{trapping rate}) \text{ vs. } 1/T, \quad (3)$$

$$\log_{10} (\text{steady-state rate}) - \frac{1}{2} \log_{10} T \text{ vs. } 1/T, \quad (4)$$

$$\log_{10} (\text{steady-state rate}) - \frac{1}{2} \log_{10} T - \gamma \log_{10} P \text{ (in mm)} + 1 \text{ vs. } 1/T. \quad (5)$$

Note that the successive corrections applied by subtracting $\frac{1}{2} \log_{10} T$ and $\frac{1}{2} \log_{10} T + \gamma \log_{10} P$ straighten out these curves in a surprising manner.

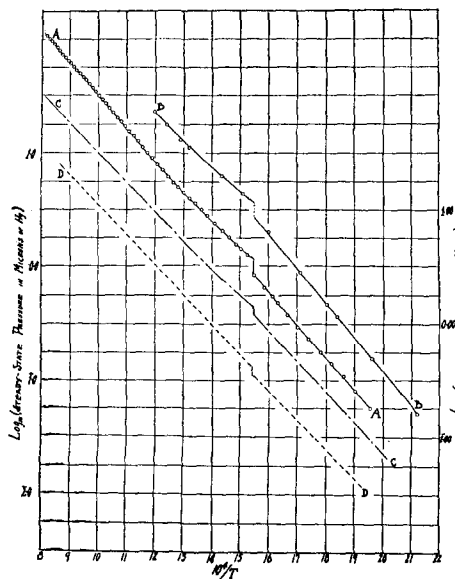


FIG. 3. Diffusion of hydrogen through commercial nickel. Sample XII. 38 mil. AA, \log_{10} (steady-state rate) vs. $1/T$; BB, \log_{10} (trapping rate) vs. $1/T$; CC, \log_{10} (steady-state rate) $-\frac{1}{2} \log_{10} T + 1$ vs. $1/T$; DD, \log_{10} (steady-state rate) $-\frac{1}{2} \log_{10} T - \gamma \log_{10} P$ (in mm) $+1$ vs. $1/T$.

The various values of the constants used in several types of diffusion formulae are given in Table I for these two samples.

Figure 5 shows the logarithm of the diffusion rate of hydrogen through anode nickel* plotted against the reciprocal of the absolute temperature. Fig. 5 also shows the variation of the isotherm slope as a function of T before the sample has been completely purified by the diffusing hydrogen. Note that the maximum occurs at the Curie point within our experimental error. These slopes of the isotherms appear in the diffusion equation as P^γ , where γ is the value of the isotherm slope as described in experimental procedure. Table II shows the constants in several types of diffusion equations for anode nickel.

After several months running this sample of anode nickel showed that the variation of the isotherm slopes from 0.5 was not as great as that shown in Fig. 5. It was found that the slopes

* This anode nickel was kindly furnished by the International Nickel Co. According to information received from their laboratories this is the purest nickel they have been able to make up to the present time. Complete chemical analyses of this type of nickel are not available, but we have been assured that this metal is at least 99.99 percent pure.

remained 0.5 within 10° of the Curie point and then showed a slight variation to about 0.53 at the Curie point.

A new sample of anode nickel 42 mils in thickness was installed and after several months running with hydrogen diffusing through the sample it was found that the deviation of the isotherms from the 0.5 law (i.e., $R \propto P^{\frac{1}{2}}$) apparently occurs only near the Curie point and there is no variation from 0.5 except possibly within 3° above this point. Fig. 6 shows the log of the rates plotted against $1/T$ for this sample in the neighborhood of the Curie point. A small variation is apparent in the region directly above the temperature 360°C .

A very careful attempt has been made from the data obtained from the last diffuser (42 mil) to find if the plot of $\log R$ vs. $1/T$ is really linear between 360° to 1060°C . It has been found that the plot is not linear and $\log_{10} R - \frac{1}{2} \log_{10} T$ must be plotted against $1/T$ in order to obtain a linear relation. This is shown in Fig. 7. As mentioned before, this diffuser was in the system long enough so that the diffusion rates were completely reproducible and the variation of the isotherm

TABLE 1. Diffusion constants for hydrogen through commercial nickel.*

EQUATION	ABOVE CURIE	BELOW CURIE
SAMPLE NO. XIII		
$D = k_1 P^{\frac{1}{2}} \exp(-b/T)$	$b_1 = 6680$	$b_1 = 6780$
	$k_1 = 0.93 \times 10^{-2}$	$k_1 = 1.02 \times 10^{-2}$
$D = k_2 P^{\frac{1}{2}} T^{\frac{1}{2}} \exp(-b/T)$	$b_2 = 6280$	$b_2 = 6440$
	$k_2 = 1.7 \times 10^{-4}$	$k_2 = 2.42 \times 10^{-4}$
SAMPLE NO. XII		
$D = k_1 P^{\frac{1}{2}} \exp(-b/T)$	$b_1 = 6650$	$b_1 = 6590$
	$K_1 = 2.0 \times 10^{-2}$	$k_1 = 1.9 \times 10^{-2}$
$D = k_2 P^{\frac{1}{2}} T^{\frac{1}{2}} \exp(-b/T)$	$b_2 = 6200$	$b_2 = 6200$
	$k_2 = 4.0 \times 10^{-4}$	$k_2 = 5.3 \times 10^{-4}$

* In all of the above equations, D is the rate of diffusion of hydrogen measured in cubic centimeters at N.T.P. per square cm area per millimeter thickness per second. P is the impressed pressure of the gas in millimeters of mercury.

slopes from $+0.5$ were at a minimum. This proves experimentally the complete diffusion equation, Eq. (1), above the Curie point and doubtless below that point also, but the lower temperature range is not sufficient to determine the exponent of T with certainty.

Figure 8 shows the experimental results of Craninsky² and Ham³ obtained with relatively pure nickel obtained from Baker & Co. The existence of an offset at the Curie point in the

diffusion isobars is clearly indicated by the results of these investigators.

The hysteresis at the Curie point for commercial nickel may be observed in Fig. 9. It should be noted that the rate obtained by the steady-state method enables one to follow this transformation under various conditions, and moreover, the method gives a clear insight into the behavior of this point when no magnetic field is present. The observations were taken for various speeds of heating through the transformation and it should be emphasized that even with very slow rates of heating (or cooling) a hysteresis is observed which can only be minimized by slowly working back and forth through the region until the transformation point is closed in between two temperatures. If readings are taken too fast the lower phase can be carried into the upper region for about 100° while the upper phase can only be brought for a much shorter distance into the lower, say about 25° . This latter effect is difficult to study because of the slow cooling rates of the furnace at these temperatures. The hysteresis for pure anode nickel seems to be considerably smaller than that shown in Fig. 9.

The possible effect of hydrogen concentration on the Curie point was studied by determining isobars at various pressures. No change in the position of the Curie point could be found for pressures from 1 atmosphere to 0.5 cm Hg.

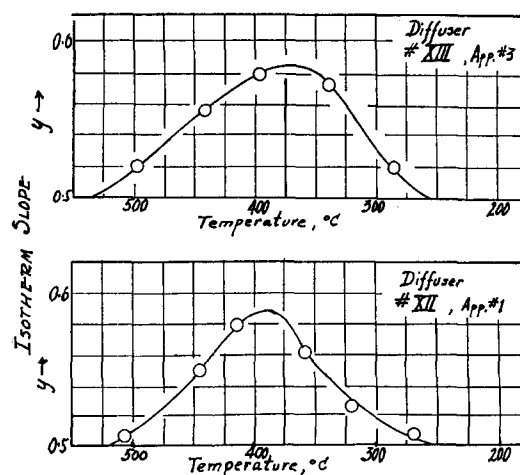


FIG. 4. Variation of isotherm slopes for commercial nickel. Samples XIII and XII.

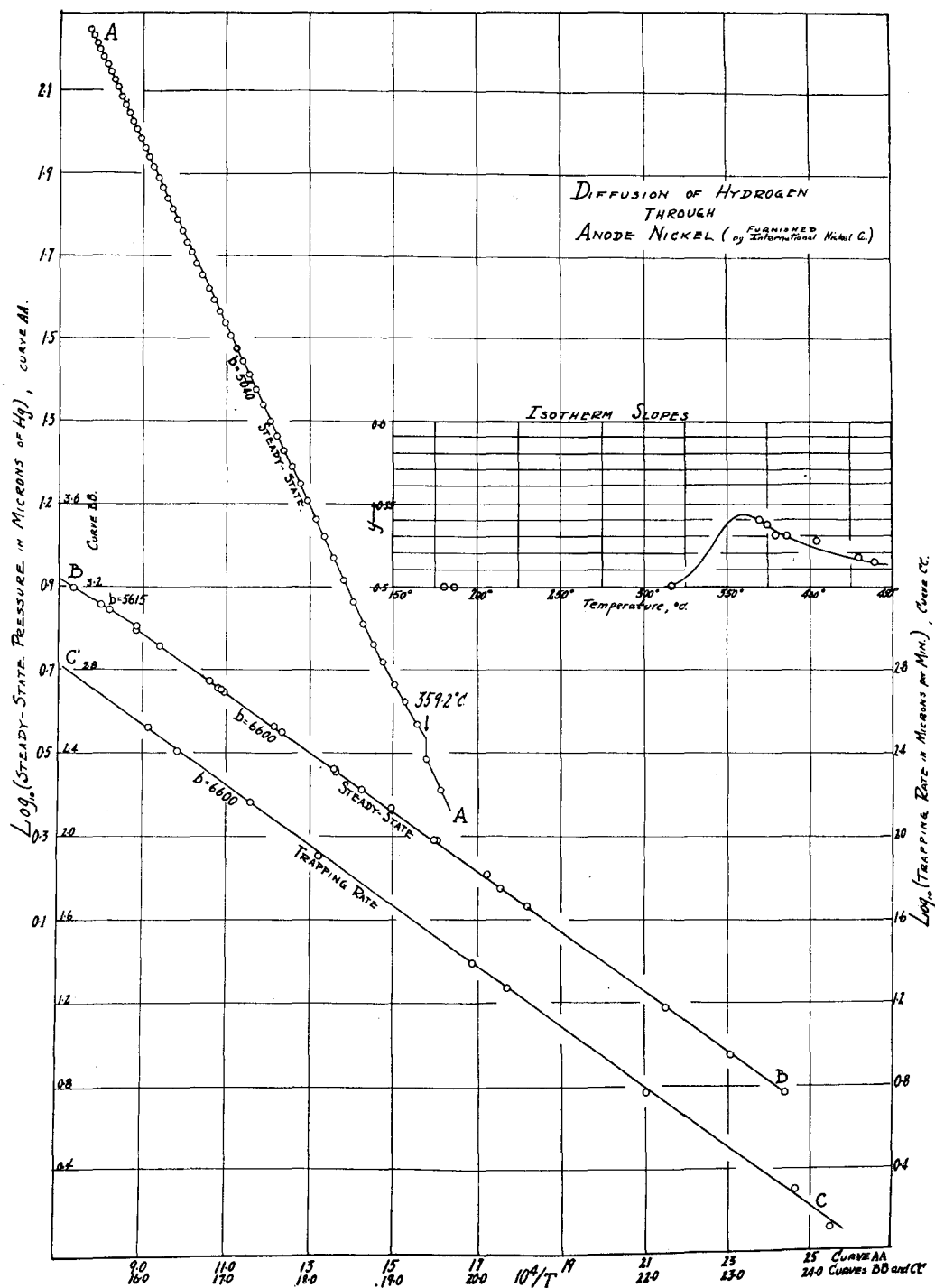


FIG. 5. Diffusion of hydrogen through anode nickel. 22 mil. AA, \log_{10} (steady-state rate) vs. $1/T$; BB, \log_{10} (steady-state rate) vs. $1/T$ for lower temperature runs; CC, \log_{10} (trapping rate) vs. $1/T$ for low temperatures.

DISCUSSION OF RESULTS

The first fact to be noted from this research on the diffusion of hydrogen through nickel is that a series of anomalies in the diffusion isobars as found in iron¹ do not exist in nickel. The same apparatus and technique as used in I was used here, consequently we must assume that the Rydberg series found in iron is truly characteristic for hydrogen diffusion through iron. While the constants given in Table I for the diffusion of hydrogen through commercial nickel are quite accurate they vary considerably with the different samples, and it has been found that these constants vary considerably with the life history of a particular sample.

The isotherms for hydrogen through nickel do not have a slope of 0.50 near the Curie point unless the nickel has been thoroughly decarburized by hydrogen diffusion. Information from the International Nickel Company indicates that minute quantities of carbon were present in the anode nickel at the start. All evidence in the data for both iron and nickel is that the explanation given by Smithells and Ransley⁷ for a deviation from 0.5 of the slope for hydrogen diffusion isotherms for iron or nickel is completely erroneous, their explanation being that the variation is due to surface conditions. On the other hand, there is nothing that contradicts the opinion expressed by Ham³ that this deviation from 0.5 is due to the simultaneous application of two or more mass action effects, or in simple terms that some of the diffusing hydrogen may be associated with an alloying element (often carbon) in the metal in pairs or ions (or as H_2^+). This also appears to be the case if the metal is alloyed with N or O.

The proof of this is that isotherms for carbonyl irons are much above a 0.5 slope in the region of 500°C until the carbon is removed whereupon they approach 0.50. In the case of pure nickel, isotherms that were considerably above 0.50 are completely reduced to 0.50 by a process recog-

TABLE 2. Diffusion constants for hydrogen through anode nickel.

EQUATION	ABOVE CURIE	BELOW CURIE
$D = k_1 P^{1/2} \exp(-b/T)$	$b_1 = 5615$ $k_1 = 3.3 \times 10^{-2}$	$b_1 = 6600$ $k_1 = 0.17$

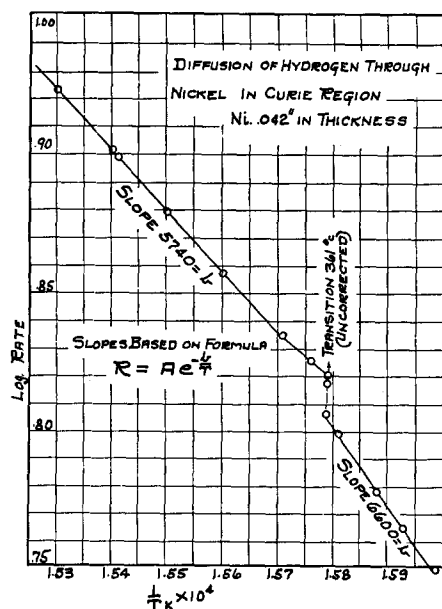


FIG. 6. Diffusion of hydrogen through nickel in the Curie region, 42 mil. Slopes based on Formula $R = A \exp(-b/T)$.

nized as a decarburizing process. The material upon which Smithells and Ransley base their theory to explain the deviation of the isotherms from the $P^{1/2}$ law had not been decarburized. In all the ranges of temperature they discuss in the case of iron and nickel we have found almost

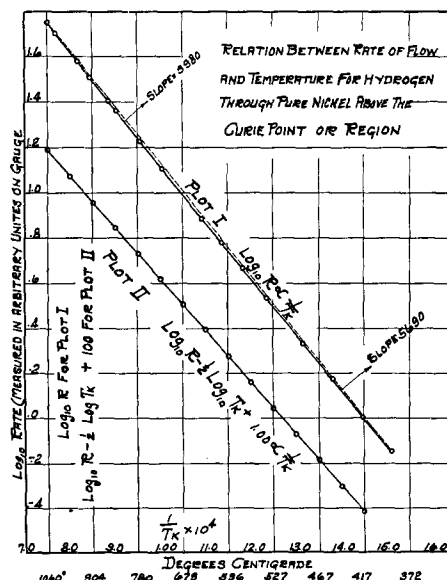


FIG. 7. Relation between diffusion rates and temperature for hydrogen through pure anode nickel above the Curie point.

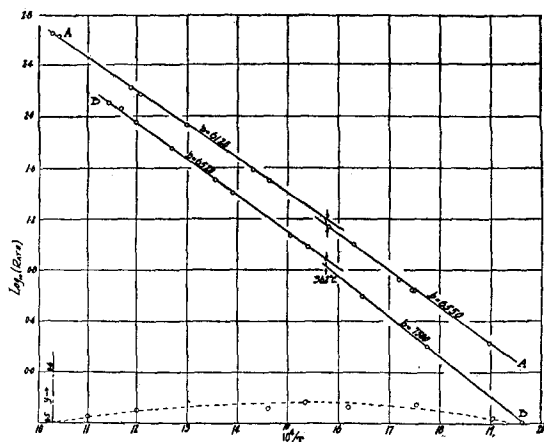


FIG. 8. Diffusion of hydrogen through Baker nickel, Craninsky² and Ham.³

perfect agreement in the variation of diffusion rate with the square root of pressure ($P^{1/2}$ law), provided the carbon is completely removed. Hence, the application of the Langmuir absorption formula which Smithells and Ransley employed is not necessary or justified.

The experimental fact that the exponent of T in the diffusion equation is $+\frac{1}{2}$ is an important theoretical point in connection with the energy of the hydrogen in the gas phase and in the metal. From this the hydrogen atoms appear to possess very nearly the same energy within the metal as without, and if the hydrogen is tightly bound to lattice points during most of its residence within the metal, because of the proton's light mass as compared to the metal atom of the lattice, but little energy of translation is allowed for the hydrogen. Its energy must be either vibrational or rotational or both. The reason that breaks indicating this rotation show in data on iron and do not in nickel may be because the latter has a relatively larger number of free electrons at any particular temperature as indicated by conductivity data, and the number of rotational states in which the hydrogen protons may exist at a particular temperature is correspondingly greater, thereby smoothing out the diffusion isobar.

The abrupt appearance of the offset at the Curie point as shown by hydrogen diffusion studies is surprising in view of the existing theories of ferromagnetism. It was for this reason that the lower portions of the curves

below the Curie point were observed with great care to ascertain whether a small bowing of the curves below the Curie point existed. If the electronic shifts necessary to cause demagnetization are governed by a statistical distribution, the fact that we are able to detect the transition at the Curie point would lead one to expect that we should be able to follow any trend or shifting due to temperature below the Curie point. Such a trend has not been found and if it does exist the magnitude is almost negligible because we have found the rates below this point to follow the same kind of diffusion law as the rates above. Evidently the intrinsic magnetism of the nickel atoms must be governed by forces which break suddenly. The above arguments, of course, refer only to demagnetization caused by temperature effects in the absence of a magnetic field.

To be specific, the theory of Slater⁸ needs modification since this theory assumes a gradual rearrangement, as the metal is heated from absolute zero, of electrons in the third shell of the nickel atom, this rearrangement increasing rapidly as the Curie point is approached. The diffusion data indicate that such cannot be the

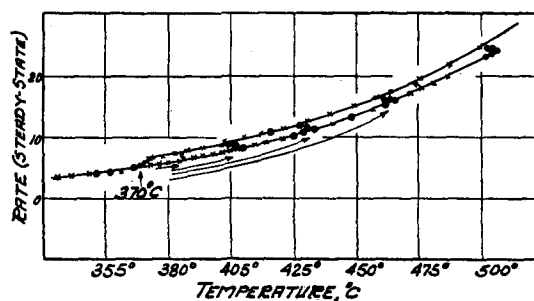


FIG. 9. Hysteresis at the Curie point in commercial nickel determined by steady-state methods.

case since the isobars are straight from 153° to 360°C.

A detailed picture of the nature of the Curie transformation is that certain atoms of the lattice must temporarily possess an additional valence electron during the transition, no doubt obtaining it from the 3d shell. This additional electron is necessary to interpret the behavior of the isotherms on pure anode nickel in the range

⁸ J. C. Slater, Phys. Rev. **49**, 537 (1936); **49**, 931 (1936).

within 3° of the Curie point. However, this condition does not persist and evidently another valence electron drops back into the $3d$ shell and has such a spin that the electrons in the $3d$ level are now paired. When this has occurred the element may be considered as paramagnetic.

CONCLUSIONS

(a) The diffusion of hydrogen through nickel has been investigated from 1100° to 150°C with both commercial and pure anode nickel. Constants in the diffusion equations have been obtained.

(b) The Rydberg series found in iron has not been found in nickel. The same apparatus as used in I was used here.

(c) The isotherms are found to vary from 0.5 in the neighborhood of the Curie point for pure anode nickel. When this nickel has been fully decarburized by exposure to diffusing hydrogen for long periods this variation from 0.5 only occurs within 3° of the Curie point.

(d) The exponent of T in the diffusion equation $R = AT^2P^{\frac{1}{2}} \exp(-b/T)$ has been found to be $+\frac{1}{2}$ for the diffusion isobars from 360° to 1050°C .

(e) The magnetic transition of nickel as shown by diffusion is abrupt, the isobars below the Curie region being as straight as those above.

(f) There is always a sudden drop in the value of B , as calculated from the simple equation

$R = A \exp(-b/T)$, at the Curie point, the value changing in the purest nickel from 6600 to 5800 with rising temperature.

(g) The Curie region shows marked hysteresis and is similar to the Curie region of pure iron in this respect.

(h) The explanation prepared by Slater to account for the effect of temperature on ferromagnetism seems to require serious modification inasmuch as the Curie transition for nickel appears to take place about as abruptly as the body-centered-face-centered transition in iron.

(i) A variation in hydrogen concentration in nickel near the Curie point does not change the position of the Curie point to a measurable amount.

(j) The loss of magnetism at the Curie transition is essentially an atomic phenomenon and should not be associated with conditions in aggregates of atoms or atomic domains.

(k) During the Curie transformation for a finite time there appears to be an additional electron in the valence shell of some nickel lattice points.

(l) A possible description of the process of the change from the ferromagnetic to the paramagnetic condition in the transition elements is that an electron is moved from the $3d$ shell to one of the 4-levels followed more or less quickly by the drop of another 4-level electron back to such a $3d$ shell as to result in pairing of electron spins in the $3d$ shell.