Diffusivity of Hydrogen in Pure Iron

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The rate of permeation of hydrogen through a highly purified iron (Ferrovac E) was measured over a pressure range of 1/30 to 300 atm. and a temperature range of 126° to 693°C. The effect of cold working of the annealed metal and of hydrogen purity were also studied. Permeability, diffusivity, and solubility were obtained from the data. Permeation rate was linear with square root of fugacity rather than pressure. No difference in ϕ or D between the annealed and cold worked tube was observed. Log *D* vs. 1/*T* was linear over the whole range of temperature, in disagreement with recent work showing a break in the plot at about 400°C. The calculated activation energy was lower than values reported in the literature. Solubility agreed well with most previous work and did not show the break in the solubility vs. temperature curve found by some recent investigators. No ageing effect was observed nor any difference between the two grades of hydrogen. All the evidence shows that diffusion through the metal is the controlling rate process in this case.

The permeation of gases through metals is a phenomenon of considerable practical importance. The special case of hydrogen and steels has been extensively studied because of the attack by hydrogen at elevated temperatures and the embrittlement caused by it even at ambient temperatures. Two papers dealing with the effect of hydrogen on the structure and the tensile properties of a wide variety of metals have been published from this laboratory (*22*, *27*). The present paper is concerned with the more fundamental question of mechanism and rate of penetration of hydrogen through a metal.

DEFINITION OF TERMS AND QUANTITIES

To avoid confusion it is well at this point to define some of the terms and quantities commonly but often loosely used in describing the movement of gases through metals. The term "permeation" will be used to describe the overall process of passage of the gas from one side of a metal barrier to the other.

A constant known as the permeability has been defined in various ways. For example one may define it for a steady state condition by the equation

$$\phi = \frac{Q\,\Delta x}{A\,\theta\,\Delta p} \tag{1}$$

where Q the quantity permeating across a membrane of thickness x under a pressure gradient Δp can be in mass or volume units but is usually expressed as mililiters at standard conditions. Values of ϕ quoted in the literature are for a certain set of standard values of the variables in Equation (1). Another definition of permeability will be given after the diffusivity is defined:

$$R = \frac{2\,\pi\,L\,D(C_1 - C_2)}{\ln\left(\dfrac{r_2}{r_1}\right)} \tag{2}$$

D can be determined from this equation but C is difficult to measure, and other measures have been developed to circumvent this difficulty. In this work the time-lag method of Barrer (*4*) was used. The time-lag equation for hollow-cylinder geometry is

$$\theta_L = \frac{r_1^2 - r_2^2 + (r_1^2 + r_2^2)\ \ln\left(\dfrac{r_2}{r_1}\right)}{4\,D\ln\left(\dfrac{r_2}{r_1}\right)} \tag{3}$$

θ_L is the intercept on the time axis of the steady state portion of a graph of quantity diffusing Q vs. time.

The solubility of a diatomic, elemental gas in a metal is expressed by

$$C = S\,\sqrt{p} \tag{4}$$

an equation often referred to as *Sievert's law*. S is a constant whose value depends on the temperature and the units. If equilibrium can be assumed between the molecular gas and the concentration of gas atoms in the metal (this assumes of course that the surface reactions are rapid relative to the diffusion so that the latter is controlling), one may combine (2) and (4) to give

$$D = \frac{R\,\ln\left(\dfrac{r_2}{r_1}\right)}{2\,\pi\,S\,L\,(p_1^{1/2} - p_2^{1/2})} \tag{5}$$

and this offers a simple means of obtaining D.

Now by analogy to the diffusivity define the steady state permeability for the case of the hollow cylinder by the equation

$$\phi = \frac{R\ln\dfrac{r_2}{r_1}}{2L(p_1^{1/2} - p_2^{1/2})} \tag{6}$$

Comparing (5) and (6) one sees that

$$D = \frac{\phi}{S} \tag{7}$$

This is true only for the case where the diffusion through the metal wall is the controlling rate, and surface resistances to permeation are negligible. This equation has often been used to calculate D from measurements of permeability, but in this paper it will be used to calculate S.

Equations (4), (5), and (6) are satisfactory if the pressure is not too high. For high pressures it is probable that the pressure should be replaced by the fugacity, and evidence for this will be presented later. ϕ, S, and D are functions of temperature, and the usual exponential equations will be assumed to represent the relationships.

SCOPE OF PRESENT WORK AND REVIEW OF PREVIOUS WORK

There is an extensive literature on the subject of the permeation of gases through metals which except for some recent work is summarized in the monographs by Barrer (*5*), Jost (*18*), Crank (*10*), and in two books (*1*, *2*), published by the American Society for Metals. The authors' own work was limited in scope to the following conditions:

1. Specimen of very pure iron.
2. Effect of pressure and temperature on diffusivity. The pressure was varied from 1 cm. Hg to 300 atm. and the temperature over the range 126° to 693°C.
3. Effect of cold-working on the diffusivity.
4. Effect of gas purity. (Two grades of hydrogen were used, one of 99.985% purity and the other 99.64%).

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Much of the work reported in the literature has been performed on iron alloys whose composition and structure were not closely reproducible so that the results tend to lack generality. It seemed desirable to reduce the number of variables by approaching as closely as possible a single solid component and obtaining as reproducible a structure as possible (short of using a single crystal) by working with pure iron in a thoroughly annealed condition. After the work was completed, Stross and Tompkins (*25*) and also Johnson and Hill (*17*) reported diffusivities for specimens of vacuum-cast iron comparable in purity to that which was used.

Both of these pairs of investigators charged cylindrical specimens with hydrogen either by heating them in the gas at atmospheric pressure and a high temperature or at elevated pressure and lower temperature and then determined D from measurement of the rate of gas evolution. Johnson and Hill reported a break in the curve of log D vs. $\frac{1}{T}$ at 200°C. Above this temperature the slope gave an activation energy of $-3,200$ g. cal./g. mole and below it $-7,820$. This means that diffusivities at ambient temperatures which have frequently been obtained by extrapolating the results at elevated temperatures may be in error by at least an order of magnitude.

Very little work has been done at elevated pressures, and the published information on the effect of pressure is conflicting. Baukloh and Guthmann (*6*) found the permeation rate for hydrogen in various steels at constant temperature to increase linearly with square root of pressure up to 40 to 100 atm. and then to become essentially constant. For nickel the rate leveled off at 20 atm. At pressures well below 1 atm. there is a departure from linearity, but the discussion of this low-pressure region is outside the scope of this paper. Naumann (*21*), who worked with various steels at pressures up to 1,000 atm. over a wide temperature range, found a linear relation between permeation rate and $\sqrt{p}$ up to the highest pressure (except for the departure in the region of very low pressure). Note that the permeation rate and the pressure should show a square-root relationship according to Equation (*6*) [except where deviations from the ideal-gas law occur, as will be shown later], only for the case where equilibrium is approached at the gas-metal interfaces, since this was an assumption necessary for the derivation of (*6*).

Although the effect of temperature has been measured a number of times, there is rather poor agreement between values of the activation energies E_P and E_D. It seemed desirable therefore to determine this quantity for pure iron, since this should be a more fundamental and reproducible quantity than the corresponding value for alloys.

It is well known that iron and steels in a cold-worked or strained state may absorb many times as much hydrogen as the same metal in an annealed state. This was thought at one time to be due to the recombination of hydrogen atoms and the storage of molecular hydrogen in internal cracks or other lattice imperfections present in strained metal. Other explanations have recently been advanced (*15, 23*). The effect of straining on the permeation rate or the diffusivity has been little studied, and again the evidence is conflicting. Rhines (*2*) reports that cold-working increases the rate but cites no supporting evidence. Baukloh and Wenzel (*8*) reported that quenching a low-carbon steel reduced the rate. Several investigators (*7, 11, 24*) found that grain size had no effect on the rate, but other investigators found the rate to increase with grain size (*6*) and still others (*20*) found the opposite effect. Increase in grain size was usually brought about by annealing.

Hill and Johnson (*14*) measured the absorption (this term is used in preference to solubility because in some highly strained metal most of the hydrogen is believed to be trapped in some way and only a small amount is present in true solution in the lattice) and diffusion of hydrogen in low-carbon steels and some binary iron-carbon alloys, cold-worked to 30% R.A. (reduction of area) and to 60%. Specimens charged with hydrogen to 15 ppm. showed no loss of gas at room temperature after 511 days. This corresponds to a D of less than 10^{-12} sq. cm./sec., which is to be contrasted with D of about 10^{-5} for annealed pure α iron and low-carbon steel obtained by extrapolation of the data at higher temperatures. They also found that the absorption decreased with increase of temperature over the range of 250° to 400°C. which is the opposite of the effect on the solubility. The pressure effect did not follow the square-root law, and absorption was quite sensitive to carbon content. They stated that they confirmed the observation of Keeler and Davis (*19*) that the absorption of hydrogen in pure iron (as contrasted with iron-carbon alloys & steels) is unaffected by cold working. D in an iron-carbon alloy was decreased many fold in the temperature range of 250° to 400°C. by cold working, but since absorption increases by approximately the same factor, the permeability should remain constant.

EXPERIMENTAL METHOD

The permeation rate was measured by maintaining a constant pressure of hydrogen inside a tubular specimen which was placed in an evacuated jacket. The gas permeating the tube wall was transferred by a mercury-diffusion pump to a constant-volume container where the increase of pressure was measured as a function of time. The permeation tube was maintained at constant temperature in a manually-controlled electric furnace. The constant high pressure of hydrogen was easily maintained within ± 0.5% by withdrawing the gas from a storage system of relatively large volume. A schematic diagram of the apparatus is shown in Figure 1. With the aid of the accompanying legend this should be self-explanatory.

The tube was constructed by boring a solid cylindrical bar of vacuum-cast Ferrovac-E, a highly purified electrolytic iron. An analysis supplied by the company showed that the sum of the maximum

TABLE 1. PERMEATION CONSTANTS FROM THE SQUARE-ROOT PLOTS

Runs	Temperature, °C.	B, ml./min.-lb./sq. in.$^{0.5}$	$\sqrt{f_o}$, lb./sq. in.$^{0.5}$
	Cold-worked tube		
9-15	291	0.00392	1.7
16-18, 25	291	0.00367	1.7
19-24	374	0.00998	1.3
1-8	375	0.00992	0.4
	Annealed tube		
113-121	126	0.0001843	0.8
103-112	176	0.000584	0.9
93-102	226	0.001465	0.7
81-92	291	0.00376	0.6
27, 64, -80	375	0.00971	0.5
28-34, 45, 46	491	0.0252	0.3
47-55	604	0.0481	0.12
35-44, 56-63	693	0.0744	0.12

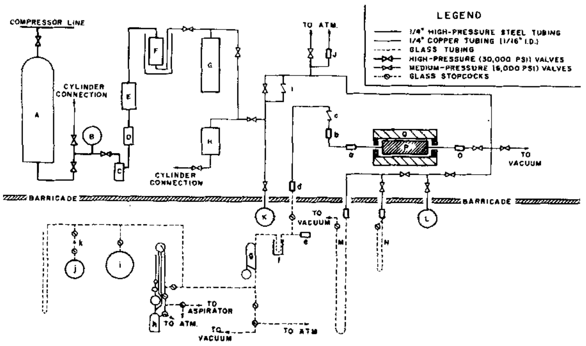

Fig. 1. Schematic diagram of gas-permeation equipment. 1. High-pressure system. A. 15,000 lb./sq. in. storage volume (0.89 cu. ft. vol.), B. 20,000 lb./ sq. in. Bourdon pressure gauge, C. oil trap containing glass wool (about 1 cu. in. vol.), D. oil filter containing glass wool, E. Drierite container (6.5 cu. in. vol.), F. charcoal container (6.5 cu. in. vol.), G. 6,000 lb./sq. in. Aminco storage vessel (0.14 cu. ft. vol.), H. 6,000 lb./sq. in. gas-holding vessel (about 20 cu. in. vol.), I. excess-flow check valve, J. rupture-disk assembly (nickel disks rated for 6,800 lb./sq. in.), K. 5,000 lb./sq. in. Heise Bourdon pressure gauge, L. 500 lb./sq. in. Heise Bourdon pressure gauge, M. 8 ft. mercury manometer, N. butyl phthalate manometer, O. coupling for disconnecting permeation tube, P. gas-permeation apparatus, Q. electric-tube furnace. 2. Vacuum system. a. soft-soldered connection from the permeation-tube vacuum jacket to the vacuum system, b. low-pressure rupture-disk assembly, c. ball type of excess-flow check valve, d. glass-to-metal coupling sealed with de Khotinski cement, e. sensing element of the Pirani gauge, f. dry ice-acetone vapor trap and Dewar flask, g. mercury diffusion pump, h. triple-scale McLeod gauge, i. gas-collecting bulb (3040.1 ml. vol.), j. detachable gas-collecting bulb (1069.6 ml. vol.), k. ground-glass tapered joint for detaching gas-collecting bulb, l. mercury manometer (32 in. height).

concentrations of eighteen impurities was of the order of 0.09%. The effective area of the tube for permeation was 130.7 sq. cm. calculated by using the logarithmic mean radius of the cylinder and a geometric mean radius of the hemispherical end. Special precautions were taken to insure concentricity of the center hole. All joints were sealed with silver solder. A high-melting solder was used for all joints except the one between the permeation tube and the vacuum jacket, where a lower melting one was used. Special precautions were taken during the soldering to prevent annealing of the permeation tube. Before machining the cast bar was cold rolled to reduce its area by 28% because it was desired to use it first in a strain-hardened condition. The original Brinell hardness of 65 was increased to 90 (55 Rockwell B).

The vacuum jacket and its closure were constructed from an austenitic stainless steel, and this was surrounded by a thick copper sleeve to reduce the temperature gradient along the length of the tube. The temperature of the diffusing gas was measured by a thermocouple inserted in a well drilled in this copper sleeve. To prevent oxidation of the sleeve and minimize permeation of air through the jacket the space in the furnace surrounding the tube assembly was continually swept with an inert gas (helium or argon).

The initial runs with the hardened tube were made at temperatures not to exceed 375°C., after which the tube was disassembled from the jacket and then reassembled with Silvaloy 850 to permit annealing of the tube and operation at higher temperatures. Annealing was carried out by holding the tube for several hours at 910°C., and examination of sections in the microscope appeared to indicate that the tube was completely annealed.

Hydrogen was stored in vessel A (Figure 1) at 9,000 lb./sq. in. from which it could be periodically bled to vessels G and H to maintain a constant pressure on the permeation tube. The check valve I prevented excessive loss of gas in case of the failure of a permeation tube or rupture of a blowout safety diaphragm. Hydrogen was purified by a train of four vessels: an oil trap, glass-wool filter, drying tube containing anhydrous $CaSO_4$, and a vessel filled with activated carbon.

Pressure in the permeation tube was measured by two Heise Bourdon gauges, one for a maximum of 500 and the other 5,000 lb./sq. in. The accuracy of the gauges was certified by the manufacturer to be about 0.1% over the entire scale and the hysteresis to be less than 0.05%. Low pressures, up to about 40 lb./sq. in. abs., were measured on a mercury manometer, and below 7 cm. of mercury the pressure was read on a butyl phthalate manometer. Pressure in the constant-volume vacuum system was read with a triple-range McLeod gauge.

The constant-volume vacuum collecting system was calibrated so that the amount of gas diffusing could be calculated at any time from a reading of the pressure and temperature and application of the ideal-gas law.

Temperature of the permeation assembly could be maintained for hours within ± 1°C. by manual control of the voltage to the heater. The temperature was measured by a chromel-constantan thermocouple which was calibrated at three fixed points. The temperature at any one point along the tube is believed to be accurate to about ± 1°C. The temperature variation along the length was about 3°C. in the worst case and usually much less for all runs made with the temperature-equalizing sleeve. In some of the earlier runs in which this sleeve was not used variations as great as 30°C. were measured, but the uncertainty in the average temperature is believed to be not over ± 5°C. Leakage of gas into the vacuum measuring system was a continual problem, and a leak-rate measurement was made before practically every run. The leakage rate was less than 1% of the permeation rate in all but one run, and it was usually less than 0.1%.

The following measurements, in addition to pressure and temperature, were made on nearly every run: rate of leakage into the gas-collecting system, time lag in reaching steady state, steady state permeation rate, volume of gas evolved from the wall of the tube during degassing between runs (Degassing between runs which took anywhere from 10 to 30 hr. was not always carried out.) The leak rate was always measured right after degassing.

A total of 121 runs was made, twenty-six of them before the tube was annealed. Metallurgical examination by photomicrographs at 100x was made of the original hot-rolled bar, of the cold-worked metal, and of small samples taken from a piece of the cold-worked metal that was placed adjacent to the permeation tube, subjected to its complete temperature history and periodically sampled for examination. This examination merely revealed that the specimen was characterized by large grains which persisted after cold working. Deformation bands were clearly visible in the cold-worked material, but these were removed and recrystallization occurred in the subsequent anneal. Examination of the surface of the tube after the experiments revealed that considerable grain growth had occurred at the ends of the tube and at a section in the middle.

DISCUSSION OF RESULTS

For each series of runs at a given temperature there was tabulated the average pressure, average fugacity, leakage rate, time lag, steady state per-

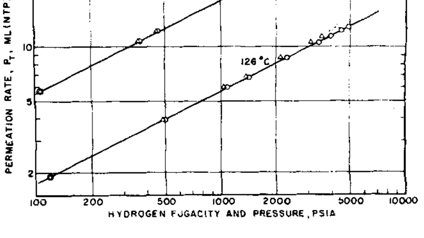

Fig. 2. Logarithmic plot of permeation rate vs. pressure and fugacity, runs 103-121.

TABLE 2. COMPARISON OF VALUES OF DIFFUSIVITIES FOR IRON AND SOME ALLOYS

Metal	Method	Reference	Temp. range, °C.	D_o, cm./sec.	E_D, g. cal./g. mole	D at 500°C. sq. cm./sec.
α-iron	Permeability and solubility	(*13*)	400-900	0.0022	2,900	3.3×10^{-4}
α-iron	Permeability and solubility	(*26*)	400-900	0.00076	2,300	1.7×10^{-4}
α-iron	Permeability and solubility	(*25*)	400-900	0.0012	2,900	1.8×10^{-4}
Carbon steel	Acid attack, time lag	(*4*)	10-100	0.0165	9,200	41×10^{-4}
α-iron	Electrolysis, time lag	(*4*)	20-80	0.011	8,740	37×10^{-4}
4.36% Ni alloy	Gas phase, time lag	(*9*)	400-900	0.0017	6,800	20×10^{-4}
α-iron	Vacuum degassing	(*25*)	150-900	0.00089	3,050	1.2×10^{-4}
α-iron	Vacuum degassing	(*17*)	25-780	0.0014	3,200	1.74×10^{-4}
α-iron	Gas phase, time lag	this work	126-693	0.000387	1,080	1.92×10^{-4}

meation rate, and total volume of gas removed by degassing. The steady state rate was usually reached within 100 min. Values of this latter rate were plotted as the logarithm vs. the pressure and also the fugacity of the hydrogen. Typical plots for the annealed tube are shown in Figure 2. The relation is almost exactly linear for fugacity, but for pressure there is a deviation at the higher pressures.

The slope of these lines for all runs on the annealed tube varied from 0.509 to 0.522 with no regular trend with temperature. In Figure 3 the rate is plotted vs. $\sqrt{f}$ for runs at two temperatures. The relation is very exactly linear but does not pass through the origin. Deviation from the square-root relation at low pressure is to be expected from previous work. Although the difference between fugacity and pressure was only 15% in the worst case, it seems to be reasonably well established by the authors' results that a better correlation is obtained with fugacity than with pressure. If diffusion is the controlling rate as appears to be the case here, the concentration of hydrogen atoms in metal in equilibrium with the gas would be expected to be related to the fugacity rather than the pressure on thermodynamic grounds. A more crucial test should result if higher pressures were used.

The straight lines can be represented by the equation

$$R = B\,(\sqrt{f} - \sqrt{f_o}) \qquad (8)$$

and Table 1 gives the derived values of B and $\sqrt{f_o}$ for all the temperatures for both the cold-worked and the annealed tube. Note that the value of the intercept $\sqrt{f_o}$ shows a continual decrease with temperature increase, in agreement with the previous literature.

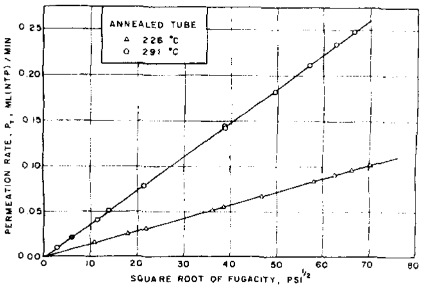

Fig. 3. Permeation rate vs. square root of fugacity, annealed tube, runs 103-121.

Calculation of permeation rates from (8) for both the cold-worked and annealed tubes at comparable temperatures shows little difference at any pressure, and it is concluded that strain produced by cold work has a negligible effect on the permeation.

No significant difference in rate of permeation was observed with the two lots of hydrogen of different initial purity. This is of interest because aging effects reported in the literature are usually attributed to impurities in the gas.

Permeability defined by Equation (1) was calculated for each of the experimental temperatures and plotted as log ϕ vs. $1/T$ yielding an excellent straight line as shown in Figure 4 for the annealed tube. The equation of the line is

$$\phi = 0.0227e^{-\frac{8,120}{RT}} \qquad (9)$$

for R in gram calories per gram mole of hydrogen and T in degrees Kalvin. The permeability calculated at 500°C. is 1.15×10^{-4}. Results of several previous investigators reported by Smithells and Ransley (*24*) for α iron gave values of ϕ_0 (value of ϕ at $T = \infty$) varying from 0.036 to 0.081, E_P from 8,950 to 11,000*, and ϕ at 500°C. from 0.54×10^{-4} to 1.78×10^{-4}. How much of this scatter in the values might be due to purity, state of strain, or surface condition of the specimens is not known, but it is hoped that the authors' values are the most representative of pure α iron.

Diffusivities were calculated from the time lag by fitting the equation

$$Q = R\,(\theta - \theta_L) \qquad (10)$$

to the steady state data to get θ_L. The accuracy of such an extrapolation of the data is not very high, since θ_L is essentially a difference between two much larger numbers. θ_L should be a function of temperature only, but there was considerable scatter of the data at a given temperature with a slight indication of a trend with pressure. Since the scatter was greatest at low pressure, only values at $p = 100$ lb./sq.in.abs. were used for calculation of D by Equation (3). A comparison of the authors' values for pure, annealed iron with those of previous investigators on pure iron and some alloys is given in Table 2. The agreement of D values at 500°C. is fairly good considering all the different methods and variables involved. The most striking disagreement between the authors' results and those of all previous investigators is the considerably smaller temperature effect. The authors have no explanation of this.

Although the values of E_P and E_D found in the authors' work are distinctly lower than values reported in the literature, their difference is in good agreement with accepted values of E_S.

The authors found no evidence of a break in an Arrhenius type of plot (Figure 4 for permeability, but an ex-

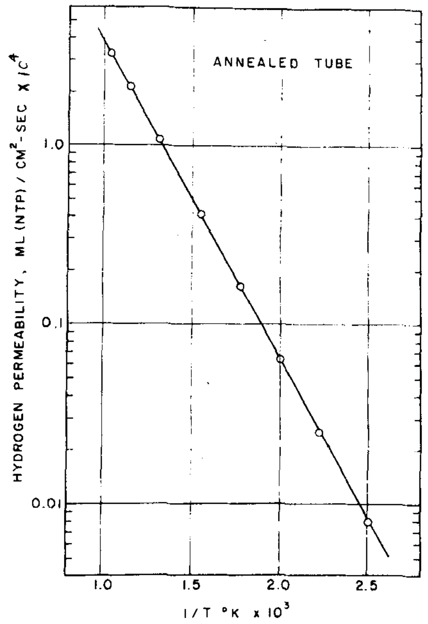

Fig. 4. Arrhenius plot showing variation of permeability with temperature.

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* Chang and Bennett (9) reported an average value of 17,800 g. cal./g. mole for E_P which is surely in error.

actly similar plot is obtained for diffusivity) when the temperature went below 200°C. In fact the authors' value of D at 126°C. fitted the straight line through the higher temperature very accurately. Stross and Tompkins (*25*) carried their experiments down to 150°C., and they found no change in slope below 200°C. Evidently more work needs to be done to explain these differences from the observations of Hill and Johnson.

The values of D for the cold-worked tube could not be obtained with quite the same accuracy as for the annealed tube, but the authors' conclusion is that cold work had little, if any, effect on D. This is in sharp contrast to the case of carbon steels where D is greatly decreased by cold working.

Assuming the diffusion process is controlling, one can calculate D from ϕ, the permeability based on the square-root-of-pressure driving force, by Equation (7), given data on solubility or conversely one can calculate solubility from ϕ and D. The authors have chosen to do the latter. Values of ϕ were calculated from the values of B [Equation (8)] disregarding the intercept $\sqrt{f_o}$.

Solubility may also be calculated from the degassing data from the equations

$$Q = \frac{C_o\left[\, r_1 - r_2 + (r_1 + r_2)\ln\left(\frac{r_2}{r_1}\right)\right]}{4\,r\left(\ln\frac{r_2}{r_1}\right)^2} \tag{11}$$

$$Q = \frac{C_o r(r_2 - r_1)}{6\ r_2} \tag{12}$$

for the hollow cylinder and hollow sphere respectively. For the derivations reference is made to Barrer (*5*), Crank (*10*), and Jaeger (*16*). Equations (11) and (12) show that the total quantity of gas evolved from the wall of the specimen should be proportional to the concentration of atomic hydrogen in the metal at the inner surface of the tube at the steady state condition just prior to degassing. If one now assumes equilibrium between gas and metal at this interface, Q should be proportional to $\sqrt{f}$ at least for the annealed tube. It can be seen from Figures 5 and 6 that this relationship holds very well. Figure 5 is for a set of the lower temperature runs and Figure 6 for higher temperatures. It might be noted that the lines in these two figures do not pass through the origin as they should if the theoretical relation were exactly followed. This deviation can be explained qualitatively as being due to the effect of surface reactions, though other explanations are possible.

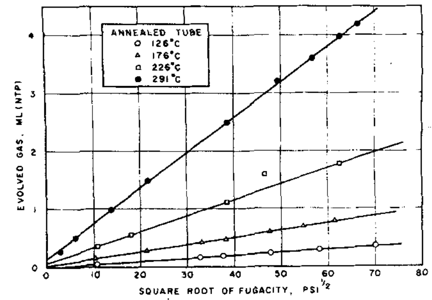

Fig. 5. Volume of gas evolved during degassing vs. square root of fugacity, annealed tube, runs 81-121.

The total gas evolved as a function of C_o for this particular tube is obtained by summing the values given by Equations (11) and (12), each multiplied by the appropriate outer area. The resulting equation is
Q (ml. at NTP) =

$$21.02\ C_o\ (\text{ml. at NTP/cc.})$$

The C_o in this equation is the same as S in Equation (4) when f is that of the gas inside the tube. Therefore from measured values of Q one can calculate S. In the literature the term "solubility" usually refers to S_1 the value at 1 atm. pressure. To compare the authors' calculated solubilities to those given in the literature it will be convenient to deal with S_1. If however one attempts to calculate S_1 directly from the degassing data, the result is very inaccurate because of the uncertainty of the extrapolation of the lines of Figures 5 and 6 to the origin. At pressures well above 1 atm. the effect of the intercepts is minimized and they can be neglected. In other words the equation

$$Q = Q_o + a\sqrt{f} \tag{13}$$

representing the lines of Figures 5 and 6 can, for this purpose, be simplified to

$$Q = a\sqrt{f} \tag{14}$$

and combining this with Equation (4) and taking f as 14.7 lb./sq.in.abs. one obtains

$$S_1 = 0.1824\ a \tag{15}$$

for S_1 in ml. (NTP)/cc. and a in $\frac{\text{ml. (NTP)}}{(\text{lb./sq.in.})^{1/2}}$.

TABLE 3. COMPARISON OF VALUES OF HYDROGEN SOLUBILITY IN α-IRON BY DIFFERENT INVESTIGATORS

Hydrogen solubility in ppm.

t, °C.	G and S	E, K, and P	Authors	H and J
585	0.942	0.932	1.14	0.795
538	0.761	0.766	0.902	0.672
490	0.590	0.608	0.682	0.559
390	0.306	0.342	0.322	0.189
290	0.129	0.156	0.131	0.253
210	0.049	0.066	0.046	0.179
145	0.017	0.026	0.015	0.0497

A comparison of values of S_1 calculated from the permeability and diffusivity by (7) and from the degassing data by (15) is shown in Figure 7 along with a line representing the data of four published investigations on solubility in α iron. The agreement is remarkably good. This provides further proof of the correctness of the assumption that diffusion is the controlling process in the case of the permeation of pure α iron by hydrogen.

The equation of the solid line in Figure 7 is

$$S_1 = 6.31\ e^{\frac{7,050}{RT}} \tag{16}$$

showing that the heat of solution is 7,050 g. cal/g. mole of hydrogen (heat absorbed). The data of Armbruster (*3*) yield a value of 6,700, in reasonably good agreement.

The data shown in Figure 7 are for the annealed tube. When the measurements on the cold-worked tube are treated in the same way, it was found that the solubility calculated from permeability and diffusivity were about the same as for the annealed tube, but the solubility based on degassing data was about 40% higher. A possible explanation for this lies in the fact that in cold-worked metal some hydrogen is trapped in a nondiffusible form, possibly by chemisorption on walls of cracks or as some chemical compound with carbon or other impurities. These and other possibilities are discussed in detail by Hill and Johnson (*15*). Podgurski (*23*) has adduced definite evidence of the formation of methane

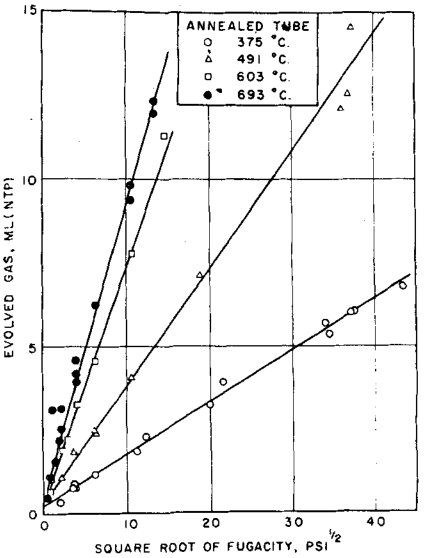

Fig. 6. Volume of gas evolved during degassing vs. square root of fugacity, annealed tube, runs 26-80.

from iron carbide in cold-worked steel at temperatures as low as 200°C. In this case however the fact that there was a difference between the annealed and the cold-worked tubes argues against the methane hypothesis since it should be formed in both cases. Whatever the trapping mechanism, it is evident that since the trapped hydrogen does not diffuse it would not affect the solubility as determined from the steady state permeation measurements, but it could appear in the degassed material and hence increase the apparent solubility. In any future work involving degassing it is recommended that the gas be analyzed.

Hill and Johnson (*15*) measured solubility of hydrogen in pure α-iron at pressures up to 136 atm. and temperatures down to 145°C. They reported abnormally high solubility below 390°C. which they stated confirmed the hypothesis of hydrogen trapping previously advanced by them (*14*). On the other hand the authors' solubilities based on the diffusivity measurements to 126°C. showed no such anomaly. In Table 3 are compared the solubilities by Geller and Sun (*13*), Eichenauer, Künzig, and Pebler (*12*), and Hill and Johnson (*15*) with the authors.

These are solubilities at 1 atm. calculated, in the first three cases, from the following equations:

$$S_1 = 42.7\ e^{-\frac{6{,}500}{RT}}$$

[Geller and Sun]

$$S_1 = 27.8\ e^{-\frac{5{,}800}{RT}}$$

[E, K, and P]

$$S_1 = 72.1\ e^{-\frac{7{,}050}{T}}$$

[Bryan and Dodge]

T is in °K. and R in $\dfrac{\text{g. cal.}}{(\text{g. mole})(°\text{K.})}$

The values for the first two sets of investigators at 145 deg. are extrapolated since their experiments did not extend to a temperature this low. The values attributed to Hill and Johnson were calculated from their tabulated values of S at 100 atm. and their values of n using the relation

$$\frac{S_{100}}{S_1} = \left(\frac{100}{1}\right)^n$$

The values of Geller and Sun, Eichenauer, Künzig and Pebler, and of Bryan and Dodge are in reasonably good agreement below 390°C. and do not confirm the abnormally high (that is higher than expected from an extrapolation of the data at temperatures above 390°C.) results reported by Hill and Johnson. Further work is desirable to find the reason for this difference.

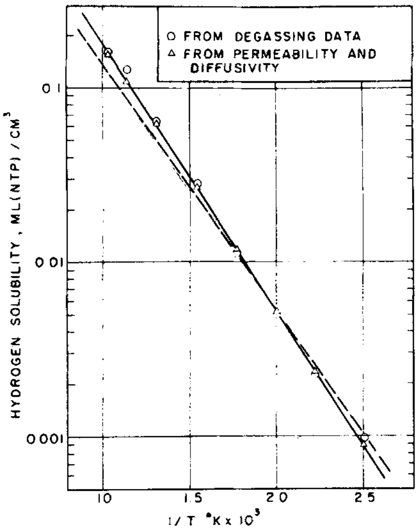

Fig. 7. Variation of solubility of hydrogen in annealed iron with temperature. The dashed line represents the best fit of four published investigations of the solubility.

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NOTATION

A = area of specimen through which gas permeates
a = empirical constant
B = empirical constant
C = concentration of gas atoms in the metal
C_o = initial concentration of gas atoms in the metal
D = diffusivity
D_o = diffusivity at $T = \infty$
E_D = activation energy for diffusion
E_P = activation energy for permeation
E_S = heat of solution
e = base of natural logarithms
f = fugacity
f_o = empirical constant
J = flux or rate of flow per unit area
L = length of cylindrical specimen
p = pressure
p_1 = pressure on entrance side
p_2 = pressure on exit side
Q = quantity permeating
R = rate of permeation or diffusion, gas constant
r = radius
r_1 = inside radius of hollow cylinder or sphere
r_2 = outside radius of hollow cylinder or sphere
S = solubility constant
S_1 = solubility of a gas at 1 atm. pressure
S_o = solubility of a gas at $T = \infty$
T = absolute temperature
x = distance in direction of permeation
Δ = finite difference
ϕ = permeability
ϕ_o = permeability at $T = \infty$
θ = time
θ_L = time lag

LITERATURE CITED

1. American Society for Metals, "Atom Movements" (1951).
2. ———, "Gases in Metals" (1953).
3. Armbruster, M. H., *J. Am. Chem. Soc.*, **65**, 1043-54 (1943).
4. Barrer, R. M., *Trans. Faraday Soc.*, **36**, 1235-48 (1940).
5. ———, "Diffusion in and Through Solids," Cambridge Univ. Press, Cambridge, England (1951).
6. Baukloh, W., and H. Guthmann, *Z. Metallkunde*, **28**, 34-40 (1936).
7. Baukloh, W., and H. Kayser, *ibid.*, **27**, 281-85 (1935).
8. Baukloh, W., and W. Wenzel, *Arch. Eisenhütten W.*, **11**, 273-278 (1937).
9. Chang, P. L., and W. D. G. Bennett, *J. Iron Steel Inst. (London)*, **170**, 205-13 (1952).
10. Crank, J., "The Mathematics of Diffusion," Oxford, Clarendon Press, England (1956).
11. Edwards, C. A., *J. Iron Steel Inst. (London)*, **110** (1924).
12. Eichenauer, W., H. Künzig, and A. Pebler, *Z. Metallk.*, **49**, 220 (1958).
13. Geller, W., and T. H. Sun, *Arch. Eisenhütten W.*, **21**, 423 (1950).
14. Hill, M. L., and E. W. Johnson, Scientific Paper 8-0160-P6, Westinghouse Research Laboratories.
15. ———, *Trans. Met. Soc. Am. Inst. Met. Engrs.*, **221**, 622-9 (1961).
16. Jaeger, J. C., *Trans. Faraday Soc.*, **42**, 615-16 (1946).
17. Johnson, E. W., and M. L. Hill, *Trans. Met. Soc. Am. Inst. Met. Engrs.*, **218**, 1104-1112 (1960).
18. Jost, W., "Diffusion in Solids, Liquids, Gases," Academic Press, New York (1952).
19. Keeler, J. H., and H. M. Davis, *J. Metals*, **5**, 44 (1953).
20. Lewkonja, G., and W. Baukloh, *Arch. Eisenhütten W.*, **6**, 453-457 (1933).
21. Naumann, F. K., *Tech. Mitt. Krupp Forsch.*, **1**, 233, p. 938; *Tech Krupp Tech. Ber.*, **6**, 77-87 (1938).
22. Perlmutter, D. D., and B. F. Dodge, *Ind. Eng. Chem.*, **48**, 885-893 (1956).
23. Podgurski, H. H., *Trans. Am. Inst. Met. Engrs.*, **221**, 389-394 (1961).
24. Smithells, C. J., and E. C. Ransley, *Proc. Roy. Soc. (London)*, **150A**, 172-197 (1953); **152A**, 706-713 (1935); **155A**, 195-212 (1936).
25. Stross, T. M., and F. C. Tompkins, *J. Chem. Soc.*, 230-34 (1956).
26. Sykes, C., H. H. Burton, and C. C. Gegg, *J. Iron Steel Inst. (London)*, **156**, 155-80 (1947); *Iron and Steel*, **20**, 591-98, 627-25 (1947).
27. Van Ness, H. C., and B. F. Dodge, *Chem. Eng. Progr.*, **51**, 266-271 (1955).

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