The Diffusion Coefficient of Hydrogen in Iron. 49.

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The diffusion coefficient D of hydrogen in iron has been evaluated in the temperature range 150-900° from measurements on the rate of evolution into a vacuum from an iron cylinder saturated with hydrogen under various conditions. Values of D are given by the equation

$$D = (5.31 \pm 0.50) \times 10^{-2} \exp [(-3050 \pm 100 \text{ cal.})/\mathbf{R}T] \text{ cm.}^2 \text{ min.}^{-1}$$

These are compared with previous results obtained by the permeation method. The present work indicates that rate-determining processes are absent at the exit surfaces of the iron, and are probably so at both exit and entry surfaces in permeation studies.

VARIOUS methods 1-14 have been used to obtain the diffusion coefficient of hydrogen in iron but only those involving the measurement of steady-state permeability rate,¹¹⁻¹⁴ and the related time-lag 10 in attaining the steady state, appear to give consistent results. In the former methods, the diffusion coefficient D is evaluated from the flux J for the diffusion of the gas through unit area of membrane from the equation

where dC/dx is the concentration gradient of the diffusing species within the metal.

The activation energies for permeation through $(E_{\rm P})$ and diffusion within $(E_{\rm D})$ the metal are defined by the equations

where P is the permeability constant, or the rate of permeation under standard conditions. Since this rate is proportional to the concentration gradient of dissolved hydrogen in the metal, $E_{\rm D}$ can be calculated from $E_{\rm P}$ and the temperature coefficient of the solubility of the gas in iron, provided that phase-boundary reactions at the iron surfaces do not control the rate.

We measured the rate of evolution of gas from a solid, iron cylinder at constant temperature into a vacuum. This method has the disadvantage that the measured rate might be sensitive to phase-boundary processes at the exit surface, but the experimental evidence points to their absence. The advantages of the method are that (i) it eliminates surface processes at the entry face in permeability measurements that might be ratedetermining; (ii) the exit surfaces of the cylinder can be kept very clean; alternatively they can be deliberately contaminated by sorption of other gases in order to test whether the evolution rate is affected by surface conditions; (iii) the solution of Fick's law for diffusion of gas (with constant D) out of a finite cylinder is available.³

EXPERIMENTAL

Materials.—Vacuum-cast rods of iron were supplied by the British Iron and Steel Research Association and contained C, 0.002; Si, 0.004; Mn, 0.005; S, 0.004; P, 0.001; Ni, 0.012; Cu,

- ¹¹ Smithells and Ransley, Proc. Roy. Soc., 1935, A, 150, 172.
 ¹² Borelius and Lindblom, Ann. Physik, 1927, 82, 201.
- ¹⁸ Ryder, Electronics, 1920, 17, 161.
- ¹⁴ Post and Ham, J. Chem. Phys., 1937, 5, 913.

¹ Tamman and Schneider, Z. anorg. Chem., 1928, **172**, 43; ² Moore and Smith, Trans. Amer. Inst. Mech. Eng., 1939, **135**, 255; ³ Andrew, Mallik, and Quarrel, J. Iron Steel Inst., 1946, **153**, 67; ⁴ Demarez, Hock, and Meuner, Acta Met., 1954, **2**, 214; ⁵ Fast, Phillips Tech. Rev., 1942, **7**, 74; ⁶ Betz, Z. Physik, 1940, 117, 100; 7 Ham and Rast, Trans. Amer. Soc. Metals, 1938, 25, 886; 8 Ham, ibid., 1937, 25, 526; Bhat and Lloyd, J. Iron Steel Inst., 1950, 165, 382.
 ¹⁰ Barrer, Trans. Faraday Soc., 1940, 36, 1235.

0.005; Al, 0.003; O, 0.0016; N, 0.0014%. Small cylinders (~ 3 cm. in length, 1.13 cm. in diam.) were machined from the rods but not polished. Hydrogen from a cylinder was purified by passage through a 30-cm. column of palladised asbestos at 300° , phosphoric oxide, and finally activated outgassed charcoal cooled in liquid nitrogen.

Apparatus.—This comprised a conventional high-vacuum system with a two-stage mercury diffusion pump, calibrated McLeod and Pirani guages, and a furnace section. Traps cooled in liquid nitrogen prevented access of mercury vapour to the iron from mercury cut-offs, etc. A transparent silica tube, 75 mm. long and of 16 mm. int. diam., formed the core of the furnace which was controlled manually within about $\pm 1^{\circ}$. Through one end of the tube was sealed a Pt/Pt-Rh thermocouple in an open silica sheath to allow the junction to be placed in direct contact with the iron cylinder. The latter was contained in a tungsten-wire cradle which was attached by silica fibres to silica-enclosed iron slugs so that the specimen could be moved in and out of the furnace by means of a magnet.

Procedure.—Before use, the iron was outgassed at 1000°, exposed to 1 atm. of hydrogen for 2 hr. at 900°, and further outgassed for 16 hr. at 1000°. For any run, the iron was saturated with hydrogen under standard conditions, *viz.*, unless otherwise stated : 1 atm. hydrogen for 16 hr. at 800° (*i.e.*, below the $\alpha - \gamma$ transition temperature), although as judged from the reproducibility of results, 2 hr. appeared to be adequate for saturation. After saturation the specimen was transferred by means of the magnet to a section of the apparatus that was cooled to -78° in a solid carbon dioxide-acetone bath; after 20 min. the hydrogen in the gas phase was evacuated.

As hydrogen is appreciably soluble in silica at high temperatures, the tube was heated to 1000° and evacuated for 2 hr. after the iron had been removed from the furnace. The temperature was then lowered to that required for the subsequent measurement of the rate of evolution, and the residual rate of outgassing into vacuum measured. The iron cylinder was then transferred from the cold trap to the furnace. Independent experiments with the thermocouple junction placed inside a cavity in the centre of the specimen showed that temperature equilibrium with the furnace was established within 6 min.

The rate of evolution was determined by a differential method, *i.e.*, by recording at convenient times the time interval Δt required for a definite pressure increase Δp at a mean pressure of 2.5×10^{-4} mm. Between measurements the evolved hydrogen was evacuated. Finally, the iron was removed and the outgassing rate from the silica tube again recorded. The results presented have been corrected for this additional rate of evolution from the silica tube.

Calculation of Results.—The solution of Fick's equation 3 for the rate of gas evolution applied to a cylinder of radius r (cm.) and length l (cm.) having an initial uniform concentration c of gas (in arbitrary units) is

if it is assumed (i) that c = 0 at $r = r_0$ for t > 0 (since the gas is evolved into a vacuum), and (ii) that D is independent of the concentration of hydrogen within the metal.

 Q_0 is the initial quantity of gas in the specimen, and K is a constant determined from its dimensions.³ For a cylinder

where β is the first root of the Bessel function of the first kind and zero order.

Since the gas was evolved into a constant volume and the increase of resistance (ΔR) of the Pirani guage was linearly related to the pressure increase Δp , then, from equation (4), the plot of $\log_{10} (\Delta R/\Delta t)$ against t (in min.) should be a straight line of gradient -0.434KD; from this, D can be evaluated in units of cm.² min.⁻¹.

Results and Discussion

Some typical plots of $\log_{10} (\Delta R/\Delta t)$ against t for various temperatures are given in Fig. 1; they show that equation (4) is valid after an initial period which, except at the highest temperatures, is longer than that required for the establishment of thermal equilibrium (~6 min.). The reproducibility of results for the gradient of the plots (-0.434KD) was usually about 4% although in some runs (cf. Fig. 2) the scatter of results was larger.

Fig. 2 shows the plot of log D against $1/T^{\circ}(\kappa)$ for one specimen from which, by the least-squares method, we obtain

$$D = 6.9 \times 10^{-2} \exp(-3220 \text{ cal.}/RT) \text{ cm.}^2 \text{ min.}^{-1}$$
 . . . (6)

From all the results obtained with six different specimens,

$$D = (5.31 \pm 0.50) \times 10^{-2} \exp \left[(-3050 \pm 100) \text{ cal.} / \mathbf{R}T \right] \text{ cm.}^2 \text{ min.}^{-1}$$
. (7)



where E_D is expressed in cal. mole⁻¹. It must be emphasised that equation (4) is only valid if D is a constant independent of the concentration of hydrogen within the metal, and rate-determining processes at the exit surface of the metal are absent.

Constancy of D.—The concentration of hydrogen dissolved in the iron was varied ninefold by saturating at 800° under various hydrogen pressures. The gradients, however, were constant within the experimental uncertainty (4%), although, of course, the heights of the maximum of the plot were different. Similarly, during any run, despite large changes in the hydrogen content of the iron, the gradient remained constant. This conclusion might have been expected because of the low solubility of hydrogen in iron so that the solution is always very dilute. Neither the temperature nor the duration of saturation of the iron with hydrogen affected the value of D at a particular temperature.

Phase-boundary Processes.—Their absence at the exit surface was confirmed by the following experiments.

(i) From the heats of adsorption of hydrogen on iron and their variation with coverage 15 we calculate that at a pressure of 1.5×10^{-2} mm. at 150°, about 25% of the iron surface should be covered with adsorbed gas, whereas at 2.5×10^{-4} mm. and 150° the coverage is less than 5%. Nevertheless, the rates of evolution into atmospheres of hydrogen at these two (constant) pressures were the same within experimental error.

(ii) Similarly, the surface was contaminated with nitrogen by using 3 cm. pressure of the gas at various temperatures from 20° to 450° after the specimen had been saturated with hydrogen. Even at the highest temperature, because of the high heat of chemisorption, 16 10% of the surface should be covered. Even so, no difference in the rates compared with that from an uncontaminated surface was found. Treatment with ammonia at 450° , thereby forming surface nitrides ¹⁷ from which the evolution of nitrogen is slow because of the high activation energy (42 kcal. mole⁻¹), was also ineffective.

(iii) Oxygen is strongly chemisorbed 16 and surface oxidation takes place below 0° ; these surface oxides are, moreover, not completely removed by reduction with hydrogen at 500°. Despite this, treatment of the iron after saturation with hydrogen with 1 cm. pressure of oxygen at temperatures between 23° and 500° had no effect, nor did preliminary repeated oxidations and reductions of the surface layers.

It is therefore concluded that the rate of diffusion within the metal was the rate-determining process and the measured rate was not associated with any phase-boundary phenomena.

The Maximum Rate of Evolution.—Application of Fick's law with a constant value of D shows that the maximum rate should be attained as soon as the sample has acquired the furnace temperature, *i.e.*, within six minutes or less after transference of the specimen from the cold trap to the furnace. Actually the rate increased to a maximum after much longer periods, the time interval being greater the lower the temperature of the evolution measurements. This initial lower rate is due to the fact that when the sample was cooled from 800°, the temperature of saturation, to -78° , hydrogen was evolved from the outer layers because its solubility is less at lower temperatures, and the rate of cooling was not sufficiently rapid to "freeze" the solubility equilibrium established at 800°. Consequently, at the commencement of the rate measurements the concentration of hydrogen in the outer layers was smaller than that in the bulk; since the cooling conditions were standardised, this lower concentration was in each case the same at the beginning of each rate measurement. It follows that the time lag before the attainment of a uniform concentration throughout the specimen, or the time, t_{\max} , which elapsed before the maximum rate of evolution was reached, is inversely proportional to the value of the diffusion coefficient at the temperature of the rate measurements. Consequently, as found experimentally, the plot of log $(1/t_{max})$ against $1/T^{\circ}(\kappa)$, though showing some scatter, is linear and from the slope of the line we calculate the temperature coefficient of D to be associated with an activation energy of 2.7 kcal. mole⁻¹, in fair agreement with the value of 3.0 ± 0.1 kcal. mole⁻¹ obtained from the gradient -0.434KD of the later, main evolution process. Better agreement is not expected since the value of t_{max} includes the variable time taken for the specimen to attain the different temperatures of the rate measurements. Some confirmation of this explanation of the position of the maxima is afforded by the increase of t_{max} and the decrease of height of the maximum when the rate of cooling was decreased, although the gradients of the later linear section of the plot were the same.

Comparison with Previous Results.-Values of D at various temperatures for the hydrogen-iron system have been obtained by applying the time-lag method ¹⁰ to the early results of Edwards¹⁸ on the rate of permeation of nascent hydrogen through iron. These are [cf. eqn. (7)] given by :

- ¹⁵ Bagg and Tompkins, Trans. Faraday Soc., 1955, 51, 1071.
- Beeck, Adv. Catalysis, 1950, 2, 151.
 Goodeve and Jack, Discuss. Faraday Soc., 1948, 4, 52.
- ¹⁸ Edwards, J. Iron Steel Inst., 1924, **60**, 9.

Later measurements,¹⁰ using activated iron, gave a lower activation energy of 6.74 kcal. Andrew *et al.*,³ using the evolution method over the temperature range 550—1100°, report $E_{\rm D}$ to be 5.75 kcal. for austenitic steels but this higher value than ours for α -iron might be expected. Demarez, Hock, and Meunier ⁴ have recently recorded values between 0.93 × 10⁻⁴ and 2.67 × 10⁻⁴ cm.² sec.⁻¹ at 650° for mild steels from rates of evolution and these are in good agreement with the value of 1.70 × 10⁻⁴ cm.² sec. calculated from equation (7) at this temperature.

There is good agreement among the results of Smithells and Ransley,¹¹ Borelius and Lindblom,¹² Ryder,¹³ and Post and Ham¹⁴ (below 900°) on the rates of permeation of hydrogen through iron. If the permeability constant P is defined as the steady-state rate in cm.³ (S.T.P.) per min. per cm.² surface through 1 cm. of iron for hydrogen on the entry side at 1 atm. into a vacuum on the exit face, their results have a mean value of

$$P = 11.3 \times 10^{-3} \exp(-9600/RT),$$

where the activation energy is in cal. mole⁻¹.

Now, provided phase-boundary processes are absent, P = -DdC/dx. Consequently, if the solubility S is expressed in units of cm.³ of hydrogen (S.T.P.) per cm.³ of iron at 1 atm.

where $S = S_0 \exp(-6700/RT)$, $S_0 = 0.156$,¹⁹ and Q, the heat of solution,¹⁸ is in cal. mole⁻¹. Hence we calculate from equation (9) that $E_D = 2900$ cal. mole⁻¹ and $D_0 = 8 \times 10^{-2}$ cm.² min.⁻¹ in good agreement with our values of 3050 cal. mole⁻¹ and 5.3×10^{-2} cm.² min.⁻¹ respectively.

There is some confusion, or inconsistency, in the literature concerning the units of the energy terms, E_P , E_D , and Q (cf. Smithells and Ransley¹¹); we have therefore consistently expressed these energies in terms of the measured quantity, *viz.*, moles of hydrogen evolved into, or taken up from, the gas phase. No assumption is therefore made about the nature of the dissolved species or of that responsible for the passage of gas through or out of the metal.

The fact that the results of permeability measurements agree well with those obtained from our values of the rates of evolution (where surface processes are proved not to be ratedetermining) suggests that phase-boundary prosesses are likewise unimportant from the kinetic viewpoint at both exit and entry surfaces in permeation measurements. Although surface treatment affects rates of permeation, the differences are small. With iron at 863° κ the ratios of the permeability constants for a polished surface and for one that has been oxidised and reduced at 800° are only 1:1.2; and even after etching the rate is increased only ten-fold.¹¹ Such comparatively small differences are probably associated with changes in the actual external surface readily accessible to the gas as distinct from the geometric area, and not due to contaminants in the surface layers.

The British Iron and Steel Association are thanked for financial support and a bursary (to J. B.).

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[Received, June 23rd, 1955.]

¹⁹ Armbruster, J. Amer. Chem. Soc., 1943, 65, 1043.