



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 gauges, 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  $-78^\circ$  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  $\Delta t$  required for a definite pressure increase  $\Delta p$  at a mean pressure of  $2.5 \times 10^{-4}$  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<sup>3</sup> 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

$$-\frac{dQ}{dt} = 32 \frac{Q_0 K}{\pi^2 \beta^2} \exp(-KDt) \quad \dots \quad (4)$$

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.<sup>3</sup> For a cylinder

$$K = \pi^2/l^2 + \beta^2/r_0^2 \quad \dots \quad (5)$$

where  $\beta$  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 ( $\Delta R$ ) of the Pirani gauge was linearly related to the pressure increase  $\Delta p$ , 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  $\text{cm.}^2 \text{min.}^{-1}$ .

## 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  $1/T^\circ (\text{K})$  for one specimen from which, by the least-squares method, we obtain

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

From all the results obtained with six different specimens,

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

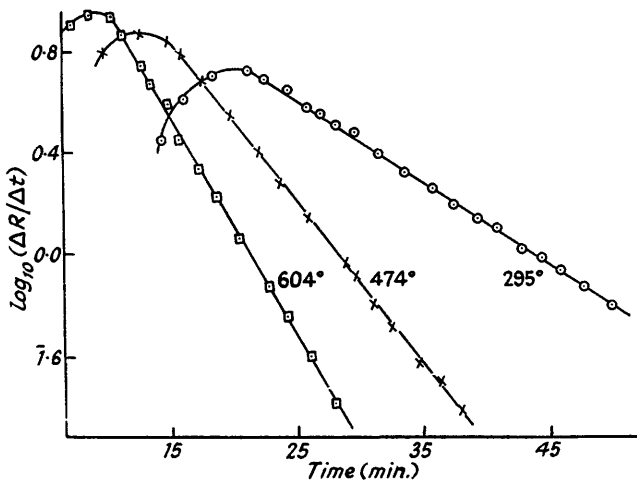
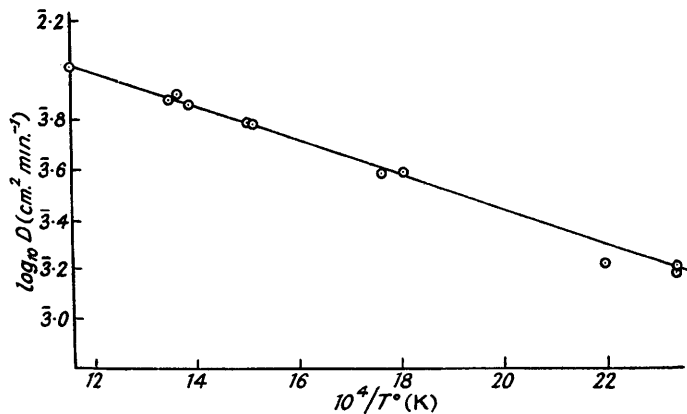


FIG. 1. Plot of  $\log (\Delta R/\Delta t)$  against  $t$ . The gradient of the linear section equals  $-0.434KD$ , where  $K$  is a constant and  $D$  the diffusion coefficient.

FIG. 2. Plot of  $\log_{10} D$  against  $1/T^\circ (\text{K})$  for one specimen.  $E = 3220 \text{ cal./mole}^{-1}$ .



where  $E_D$  is expressed in  $\text{cal. mole}^{-1}$ . 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  $800^\circ$  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.



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

There is good agreement among the results of Smithells and Ransley,<sup>11</sup> Borelius and Lindblom,<sup>12</sup> Ryder,<sup>13</sup> and Post and Ham<sup>14</sup> (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.<sup>3</sup> (S.T.P.) per min. per cm.<sup>2</sup> 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<sup>-1</sup>.

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

$$P = D_0 S_0 \exp[-(E_D - Q)/RT] \dots \dots \dots (9)$$

where  $S = S_0 \exp(-6700/RT)$ ,  $S_0 = 0.156$ ,<sup>19</sup> and  $Q$ , the heat of solution,<sup>18</sup> is in cal. mole<sup>-1</sup>. Hence we calculate from equation (9) that  $E_D = 2900$  cal. mole<sup>-1</sup> and  $D_0 = 8 \times 10^{-2}$  cm.<sup>2</sup> min.<sup>-1</sup> in good agreement with our values of 3050 cal. mole<sup>-1</sup> and  $5.3 \times 10^{-2}$  cm.<sup>2</sup> min.<sup>-1</sup> 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 Ransley<sup>11</sup>); 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 rate-determining) suggests that phase-boundary processes 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° K 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.<sup>11</sup> 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.

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IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,  
S. KENSINGTON, LONDON, S.W.7.

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<sup>19</sup> Armbruster, *J. Amer. Chem. Soc.*, 1943, **65**, 1043.