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Permeation of hydrogen through metals

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Permeation of Hydrogen through Metals†

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Abstract

The theory of permeation of hydrogen through certain transition metals has been further developed. It has been shown that this theory, in which certain slow phase-boundary processes couple with diffusion to produce the permeation phenomena, can in rather simple ways predict the observed behaviour. In particular, 'threshold pressures' for permeation can be understood; and also permeation velocities which depend on the ingoing pressure, p_1, according to $p_1{}^n$ where $0 \leqslant n \leqslant 1$, and upon membrane thickness l according to l^m where $-1 \leqslant m \leqslant 0$.

§ 1. Introduction

It is some time since the adsorption of hydrogen was first considered as a modifying influence in the permeation of this gas through metals (Smithells and Ransley 1935). The rôle of slow phase-boundary processes in permeation was considered quantitatively by Wang (1936) and by Barrer (1939, 1940). The latter of these authors was able to demonstrate the presence of slow processes for diffusion of hydrogen through hollow Pd cathodes, and to show that in successive experiments with a freshly activated Pd surface phase-boundary reactions increasingly dominated the tempo of permeation (Barrer 1940). Subsequently Wahlin and Naumann (1953) found that the rate of permeation did not vary as $1/l$, where l is the thickness of the metal membrane. Recently it has been found (Silberg and Bachman 1958) that in diffusion of hydrogen through Pd discs between 200 and 600°c the permeation rate did not vary either as $1/l$ or as $p^{1/2}$, the latter being the pressure variation expected in the simplest cases, as shown by various experiments (Barrer 1951, Toda 1958). It was then suggested that no current theory of permeation through metals could explain these experimental results (Silberg and Bachman 1958). It is the purpose of the present paper further to develop the analyses of Smithells and Ransley, Wang, and Barrer, and thus to show how far the theory of phase boundary processes coupled with diffusion is able to explain experimental observations on permeation so far made.

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† Communicated by the Authors.

§ 2. Formulation of the Problem

We consider a plate of metal bounded by planes $x = 0$ and $x = l$, the pressures p_1 and p_2 being maintained at the faces $x = 0$ and l respectively. The hydrogen undergoes chemisorption as atoms to give localized mono-layers which at equilibrium follow ·Langmuir's isotherm. Absorption into, and diffusion within, the metal occurs as atoms. The fractions of the surface covered by adsorbed hydrogen at $x = 0$ and l are θ_1 and θ_2, while the concentrations of dissolved hydrogen just inside the metal at $x = 0$ and l are u_0 and u_l respectively.

Then the following processes of adsorption, desorption, and penetration may be considered as typical, in all cases for unit area :

(a) A gas molecule strikes the surfaces, dissociates and is adsorbed as atoms :
$$\text{Rate} = k_1 p (1 - \theta)^2.$$

(b) A pair of adsorbed atoms combines and evaporates as a molecule :
$$\text{Rate} = k_2 \theta^2.$$

(c) An adsorbed atom passes into the metal :
$$\text{Rate} = k_3 \theta [1 - (u/u_s)],$$

where u_s denotes the saturation concentration of hydrogen atoms in the metal.

(d) An atom in the metal enters the surface :
$$\text{Rate} = k_4 u (1 - \theta).$$

(e) A molecule strikes the surface and dissociates, one atom staying on the surface and the other entering the metal :
$$\text{Rate} = k_5 p (1 - \theta)[1 - (u/u_s)].$$

(f) An atom in the metal enters the surface, combines with another adsorbed atom and evaporates as a molecule :
$$\text{Rate} = k_6 u \theta.$$

In the above processes the k's denote transmission coefficients for transport of atoms across the relevant interface, per unit area per unit time. In addition, within the metal there is a diffusion flux, J per unit area of membrane normal to the direction of flow, which may be written

$$J = D \frac{(u_0 - u_l)}{l} . \qquad \qquad \text{. . . . . (1)}$$

This diffusion flux in the steady state equals the net transport across any chosen interface, such as that between gas phase and adsorbed layer or that between the adsorbed layer and the metal surface. Then the following equations must be valid in addition to and simultaneously with eqn. (1):

$$J = k_1 p_1 (1 - \theta_1)^2 - k_2 \theta_1^2 + 2k_5 p_1 (1 - \theta_1)[1 - (u_0/u_s)] - 2k_6 \theta_1 u_0, \qquad \text{. . (2)}$$

$$J = k_3 \theta_1 [1 - (u_0/u_s)] - k_4 u_0 (1 - \theta_1) + k_5 p_1 (1 - \theta_1)[1 - (u_0/u_s)] - k_6 \theta_1 u_0, \qquad \text{(3)}$$

$$J = k_4 u_l (1 - \theta_2) - k_3 \theta_2 [1 - (u_l/u_s)] + k_6 \theta_2 u_l - k_5 p_2 (1 - \theta_2)[1 - (u_l/u_s)], \qquad \text{(4)}$$

$$J = k_2 \theta_2^2 + 2k_6 \theta_2 u_l - k_1 p_2 (1 - \theta_2)^2 - 2k_5 p_2 (1 - \theta_2)[1 - (u_l/u_s)]. \qquad \text{. . (5)}$$

J is in all cases expressed as the net number of atoms transferred across the relevant interface, per unit time per unit area. Processes (e) and (f) give rise to a factor of 2 in terms containing k_5 and k_6 in eqns. (2) and (5), since for every atom crossing the interface between the adsorbed layer and the metal, two atoms cross the corresponding interface between the gas-phase and the adsorbed layer. This factor of 2 has been omitted from earlier formulations of equations analogous to (2) and (5) above (Wang 1936, Barrer 1939) without, however, invalidating the conclusions reached, giving:

$$J' = k_1 p_1 (1 - \theta_1)^2 - k_2 \theta_1^2 + k_5 p_1 (1 - \theta_1)[1 - (u_0/u_s)] - k_6 \theta_1 u_0, \quad . \quad . \quad (2a)$$

$$J' = k_2 \theta_2^2 + k_6 \theta_2 u_l - k_1 p_2 (1 - \theta_2)^2 - k_5 p_2 (1 - \theta_2)[1 - (u_l/u_s)], \quad . \quad . \quad (5a)$$

where J' was then identified with J. For the eqns. $(2a)$, (3), (4), $(5a)$ to be internally consistent however, J' is to be regarded as the net flux of diatomic molecules across the interface between the gas-phase and the adsorbed layer, with k_1 and k_2 transmission coefficients for transport of diatomic molecules. Thus, $J' = J/2$.

From these equations by suitable rearrangement one may eliminate u_0 and u_l and obtain three relationships involving J, p_1 and p_2, the θ's, u_s, D and the various rate constants. For example, from eqns. (1), (3) and (4) one obtains

$$J \left[\frac{l}{D} + \frac{1}{\dfrac{k_3 \theta_1}{u_s} + k_4(1 - \theta_1) + k_5 p_1 \dfrac{(1 - \theta_1)}{u_s} + k_6 \theta_1} \right.$$

$$+ \left. \frac{1}{\dfrac{k_3 \theta_2}{u_s} + k_4(1 - \theta_2) + \dfrac{k_5 p_2 (1 - \theta_2)}{u_s} + k_6 \theta_2} \right]$$

$$= \frac{k_3 \theta_1 + k_5 p_1 (1 - \theta_1)}{\dfrac{k_3 \theta_1}{u_s} + k_4(1 - \theta_1) + \dfrac{k_5 p_1 (1 - \theta_1)}{u_s} + k_6 \theta_1}$$

$$- \frac{k_3 \theta_2 + k_5 p_2 (1 - \theta_2)}{\dfrac{k_3 \theta_2}{u_s} + k_4(1 - \theta_2) + \dfrac{k_5 p_2 (1 - \theta_2)}{u_s} + k_6 \theta_2} . \quad . \quad (6)$$

Thus, from eqn. (6), we may write

$$J = \frac{F_1(p_1, p_2, \theta_1, \theta_2)}{(l/D) + F_2(p_1, p_2, \theta_1, \theta_2)}, \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where F_1 and F_2 are the functions of p and θ defined by eqn. (6). If $F_2 \gg (l/D)$ then J depend on l and D only in so far as θ_1 and θ_2 depend on l and D (eqns. (1) to (5)), while if $F_2 \ll (l/D)$ then

$$J = (D/l) . F_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

and J tends to have the normal dependence on D and l, with a moderating influence due to F_1.

θ_1 and θ_2 are functions *inter alia* of p_1 and p_2, and so J may not vary directly as $\sqrt{p}$. Since there is a net flux in the x-direction, θ_1 and θ_2 will not have values corresponding to the equilibria for pressures p_1 and p_2 respectively in static systems. If, however, we approximate to θ_1 and θ_2 by assuming $k_1, k_2 \gg k_3, k_4, k_5$ or k_6 we would normally have on the basis of ideal localized adsorption (Fowler and Guggenheim 1939)

$$\theta_1 \sim \frac{a\sqrt{(p_1)}}{1+a\sqrt{(p_1)}} \; ; \; \theta_2 \sim \frac{a\sqrt{(p_2)}}{1+a\sqrt{(p_2)}} \text{ where } a = \sqrt{\left(\frac{k_1}{k_2}\right)}. \quad . \quad . \quad (9)$$

We may now consider limiting cases based on eqns. (9) and (6) and see what dependences of J upon l, p and D could be anticipated.

§ 3. Limiting Cases Based on Eqns. 6 and 9

In order to simplify eqn. (6) we will throughout assume p_2 and θ_2 to be very small. Then from eqns. (9) and (6),

$$J = \frac{k_3 a\sqrt{(p_1)} + k_5 p_1}{\left(\dfrac{l}{D} + \dfrac{1}{k_4}\right)\left[\dfrac{k_3 a\sqrt{(p_1)}}{u_s} + k_4 + \dfrac{k_5 p_1}{u_s} + k_6 a\sqrt{(p_1)}\right] + (1 + a\sqrt{(p_1)})} . \quad (10)$$

This expression can lead to various limiting cases, according to the relative magnitudes of the terms in it. Several of these are given in table 1 for the case when *D is sufficiently small*. In all instances given, the flux, J, is inversely proportional to thickness and proportional to the diffusion coefficient. J may however depend variously upon the rate constants k_3, k_4, k_5 and k_6 and upon p_1, being independent of pressure in one extreme and proportional to pressure in the other. The $\sqrt{p}$ pressure dependence of case (v) of the table is not uncommon. Cases (viii) and (ix) arise when either one or other of the two mechanisms by which hydrogen atoms can pass into and out of the metal is absent. Other limiting cases can also readily be seen, such as those arising when the term $(1 + a\sqrt{(p_1)})$ is much greater than the other terms in the denominator of eqn. (10). This can give fluxes such as

$$J = \frac{k_3 . a\sqrt{(p_1)} + k_5 p_1}{1 + a\sqrt{(p_1)}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

which are independent either of D or of l, while still giving pressure dependences in which the exponent lies *between zero and unity*, according to the relative magnitudes of the several terms of eqn. (11).

A third group of limiting cases arises when D is sufficiently large. Typical examples are summarized in table 2, in all of which *the flux is independent both of D and of thickness l*, and so the rate-controlling processes are always at the phase-boundaries. The flux may vary with pressure, however, *the exponent of pressure lying between 0 and 1 according to circumstances*. The examples given in tables 1 and 2, and in eqn. (11) are extremes: under appropriate conditions the terms l/D and $1/k_4$ in eqn. (10) may be comparable (see Discussion) and, there will then be partial dependence of the flux upon diffusion coefficient and thickness of membrane.

Table 1.   Limiting Values for J when p_2 and θ_2 are Very Small

Main condition	Subsidiary conditions	Value of J
D small enough	(i) $[1 + a\sqrt{(p_1)}] \ll l\left[\dfrac{k_3 a\sqrt{(p_1)}}{u_s} + k_4 + \dfrac{k_5 p_1}{u_s} + k_6 a\sqrt{(p_1)}\right]$	$J = \dfrac{D[k_3 a\sqrt{(p_1)} + k_5 p_1]}{l\left[\dfrac{k_3 a\sqrt{(p_1)}}{u_s} + k_4 + \dfrac{k_5 p_1}{u_s} + k_6 a\sqrt{(p_1)}\right]}$
	(ii) As for (i), and also p_1 made small enough	$J = \dfrac{D}{l} \cdot \dfrac{1}{k_4} \cdot (k_3 a\sqrt{(p_1)} + k_5 p_1)$
	(iii) As for (i), and $k_3 a\sqrt{(p_1)} \gg k_5 p_1$	$J = \dfrac{D[u_s k_3 a\sqrt{(p_1)}]}{l[u_s k_4 + (k_3 + u_s k_6) a\sqrt{(p_1)}]}$
	(iv) As for (iii), with p_1 large enough	$J = \dfrac{Du_s k_3}{l[k_3 + u_s k_6]}$
	(v) As for (iii), with p_1 small enough	$J = \dfrac{Dk_3 a\sqrt{(p_1)}}{l k_4}$
	(vi) As for (i), and with $k_3 a\sqrt{(p_1)} \ll k_5 p_1$	$J = \dfrac{Dk_5 p_1}{l\left[k_4 + \dfrac{k_5 p_1}{u_s} + k_6 a\sqrt{(p_1)}\right]}$
	(vii) As for (vi), and p_1 sufficiently small	$J = \dfrac{Dk_5 p_1}{l k_4}$
	(viii) As for (i), but with k_5 and k_6 zero	$J = \dfrac{Dk_3 a\sqrt{(p_1)}}{l\left[\dfrac{k_3 a\sqrt{(p_1)}}{u_s} + k_4\right]}$
	(ix) As for (i), but with k_3 and k_4 zero	$J = \dfrac{Dk_5\sqrt{(p_1)}}{l\left[\dfrac{k_5\sqrt{(p_1)}}{u_s} + k_6 a\right]}$

Table 2.   Additional Limiting Values for J when p_2 and θ_2 are Very Small

| Main condition	Subsidiary conditions	Value of J
D large enough	(i) None	$J = \dfrac{[k_3 a \sqrt{(p_1)} + k_5 p_1]}{\dfrac{k_3 a \sqrt{(p_1)}}{k_4 v_s} + 1 + \dfrac{k_5 p_1}{k_4 v_s} + \dfrac{k_6 a \sqrt{(p_1)}}{k_4}} + [1 + a\sqrt{(p_1)}]$
	(ii) p_1 made sufficiently small	$J = \dfrac{k_3 a \sqrt{(p_1)} + k_5 p_1}{2}$
	(iii) As for (ii), and $k_3 a \sqrt{(p_1)} \ll k_5 p_1$	$J = \dfrac{k_5 p_1}{2}$
	(iv) As for (ii), and $k_3 a \sqrt{(p_1)} \gg k_5 p_1$	$J = \dfrac{k_3 a \sqrt{(p_1)}}{2}$
	(v) k_5 and k_6 are zero	$J = \dfrac{k_3 a \sqrt{(p_1)}}{\dfrac{k_3 a \sqrt{(p_1)}}{k_4 v_s} + a\sqrt{(p_1)} + 2}$
	(vi) As for (v), with p_1 small enough	$J = \dfrac{k_3 a \sqrt{(p_1)}}{2}$
	(vii) As for (v), with p_1 large enough	$J = \dfrac{k_3 k_4 v_s}{k_3 + k_4 v_s}$

§ 4. Discussion

In order to see the ways in which pressure and membrane thickness may influence the flux, J, through the metal we will consider quantitatively a small number of the possibilities. Table 1, case (ii).

$$\left\{ J = \frac{D}{l}\frac{k_3 a}{k_4}\sqrt{(p_1)}\left[1 + \frac{k_5}{k_3 a}\sqrt{(p_1)}\right]\right\}$$

and table 2, case (ii),

$$\left\{ J = \frac{k_3 a}{2}\sqrt{(p_1)}\left[1 + \frac{k_5}{k_3 a}\sqrt{(p_1)}\right]\right\}$$

Fig. 1
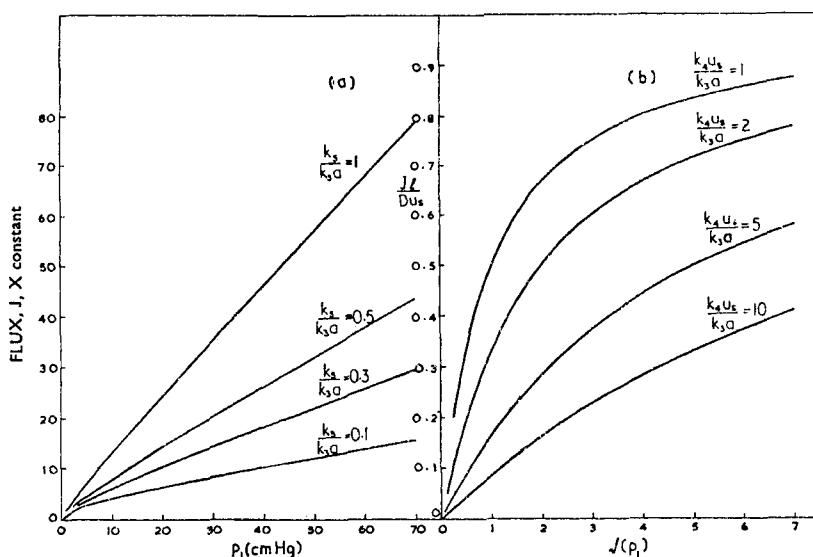
Some possible pressure dependences of the permeation rates. (*a*) The flux, J, as a function of pressure for table 1, case (ii), and for table 2, case (ii). The constant multiplying J is $lk_4/Dk_3 a$ in the former instance and $2/k_3 a$ in the latter. (*b*) Pressure dependence of the flux for table 1, case (viii).

both give the same kind of pressure dependence, which is seen in fig. 1(*a*). In this figure $J(lk_4/Dk_3 a)$ or $J(2/k_3 a)$, respectively, are shown as functions of p_1, when $(k_5/k_3 a) = 1$, 0·5, 0·3 and 0·1. The flux at low pressure is proportional to $\sqrt{(p_1)}$, but at larger pressures becomes proportional to p_1. Another kind of pressure dependence is shown by the flux according to table 1, case (viii),
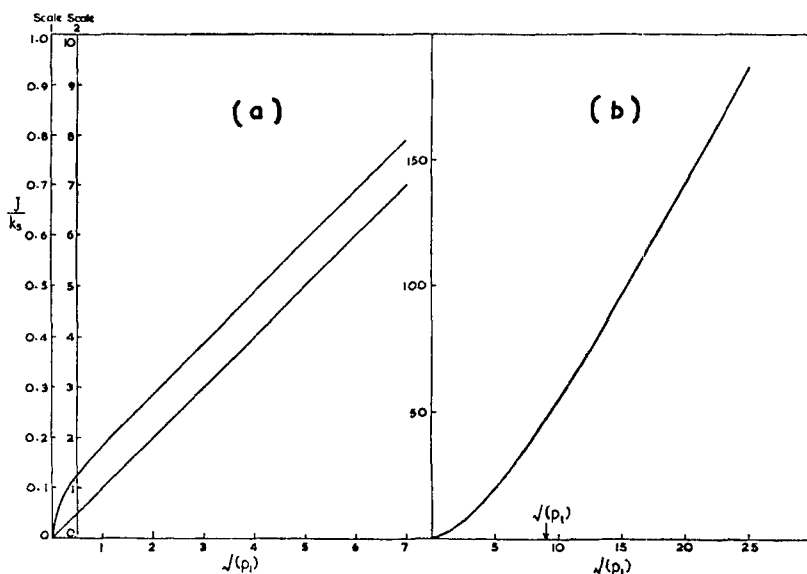
$$\left[J = \frac{Du_s}{l}\cdot\frac{\sqrt{(p_1)}}{\frac{k_4 u_s}{k_3 a}+\sqrt{(p_1)}}\right].$$

Figure 1(*b*) shows Jl/Du_s as a function of $\sqrt{(p_1)}$, taking $(k_4 u_s/k_3 a) = 1, 2, 5$ and 10 respectively. The limiting value of the flux as $p_1 \to \infty$ is Du_s/l.

As a third example of the ways in which J may vary with the pressure we may consider eqn. (11):

$$\left\{ J = k_5 \cdot \sqrt{(p_1)} \frac{\left[\dfrac{k_3 a}{k_5} + \sqrt{(p)_1} \right]}{1 + a\sqrt{(p_1)}} \right\}.$$

Fig. 2

Pressure dependence of J according to eqn. (11).
(*a*) Upper curve: $k_3/k_5 = 0\cdot1$; $a = 10$ (scale 1).
　　　Lower curve: $k_3/k_5 = 1$; $a = 1$ (scale 2).
(*b*) $k_3/k_5 = 10$; $a = 0\cdot1$.

When J/k_5 is plotted against $\sqrt{(p_1)}$ curves are obtained which may initially be concave towards the axis of J/k_5 or towards that of $\sqrt{(p_1)}$. However at higher pressures J/k_5 always becomes proportional to $\sqrt{(p_1)}$, (fig. 2(*a*) and 2(*b*)). The flux is also initially proportional to $\sqrt{(p_1)}$, the slope $dJ/d\sqrt{(p_1)}$ being $k_3 a$ when $p_1 \to 0$. On the other hand the final slope $dJ/d\sqrt{(p_1)} = k_5/a$ when $p_1 \to \infty$. The curve of J/k_5 vs $\sqrt{(p_1)}$ is thus convex towards the axis of J/k_5 if $a > \sqrt{[(k_5/k_3)]}$ and convex towards the axis of $\sqrt{(p_1)}$ if $a < \sqrt{[(k_5/k_3)]}$. This latter condition leads to the idea of a 'threshold pressure', p_t, shown in fig. 2(*b*), which is the intercept made by the asymptotic curve upon the axis of $\sqrt{(p_1)}$. Such threshold pressures have been observed in various experiments where hydrogen diffuses through metals (Barrer 1951, Toda 1958, Borelius and Lindblom 1927), but one notes that under the conditions
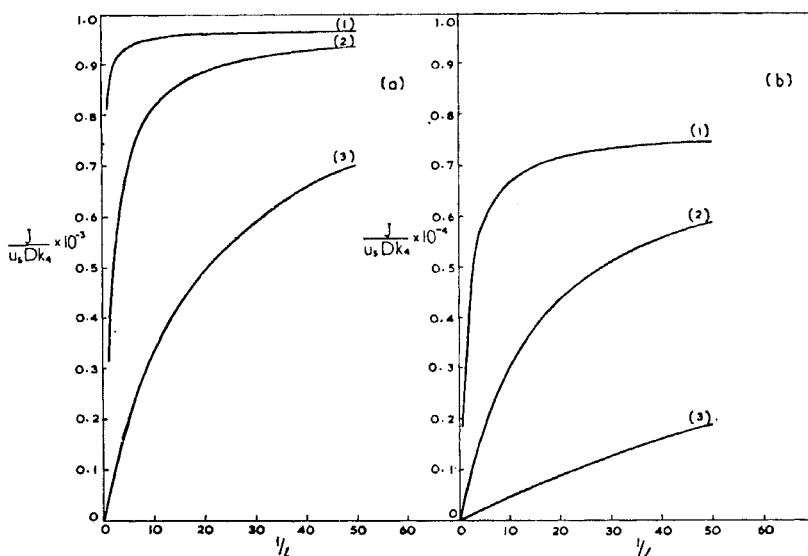
giving rise to eqn. (11) negative intercepts on the axis of $\sqrt{(p_1)}$ are also possible. The flux J in eqn. (11) can be written as

$$J = \frac{k_5}{a} \sqrt{(p_1)} \left\{ 1 + \frac{\left(\dfrac{k_3 a^2}{k_5} - 1 \right)}{[1 + a\sqrt{(p_1)}]} \right\} \quad \ldots \ldots \quad (12)$$

which, when $p_1 \to \infty$, approaches the asymptote

$$J = \frac{k_5}{a} \left\{ \sqrt{(p_1)} - \frac{\left(1 - \dfrac{k_3 a^2}{k_5} \right)}{a} \right\} \quad \ldots \ldots \ldots \quad (13)$$

Fig. 3

Dependence of J upon thickness of membrane, according to eqn. (10), but assuming that k_5 and k_6 tend to zero.

(a) For all curves, $D = 10^{-5}$ cm^2 sec^{-1}; $a = 10$; $\sqrt{p} = 10$; $u_s k_4/a k_3 = 10$; and for curves 1, 2 and 3 respectively, $k_4 = 10^{-4}$, 10^{-3} and 10^{-2}.

(b) For all curves, $D = 10^{-5}$ cm^2 sec^{-1}; $a = 1$; $\sqrt{p} = 10$; $u_s k_4/a k_3 = 10$; and for curves 1, 2 and 3 respectively, $k_4 = 10^{-4}$, 10^{-3} and 10^{-2}.

Thus the 'threshold pressure' is given by

$$\sqrt{(p_t)} = \frac{1 - \dfrac{k_3 a^2}{k_5}}{a} \quad \ldots \ldots \ldots \quad (14)$$

and $\sqrt{(p_t)}$ may have positive or negative values according as

a is $< \sqrt{[(k_5/k_3)]}$ or $a > \sqrt{[(k_5/k_3)]}$ respectively.

The effect of thickness of membrane upon the flux was examined using eqn. (10) as a starting point.   For simplicity we will assume that k_5 and k_6 tend to zero.   When l/D and $1/k_4$ are comparable in magnitude the flux can then be written in the form

$$\frac{J}{u_s D k_4} = \frac{\sqrt{(p_1)}}{(lk_4 + D)\left\{\sqrt{(p_1)} + \dfrac{u_s k_4}{ak_3}\right\} + \dfrac{u_s D k_4}{ak_3}\left[1 + a\sqrt{(p_1)}\right]}. \qquad . \quad (15)$$

Figures 3(a) and 3(b) show $J/u_s D k_4$ as a function of $1/l$ at a fixed pressure p_1. For all curves D was taken as 10^{-5} cm^2 sec^{-1}, $\sqrt{(p_1)}$ as 10 and $u_s k_4/ak_3$ as 10. The three curves in fig. 3(a) then refer in order to $k_4 = 10^{-4}$, 10^{-3} and 10^{-2} respectively, for $a = 10$.   Those in fig. 3(b) have the same values of k_4, but $a = 1\cdot0$.   In all cases, as the membrane becomes thinner, J tends to become independent of thickness, although in fig. 3(b), curve 3, J is initially almost a linear function of $1/l$.

It is thus seen that the theory of coupled diffusion and phase-boundary processes can offer simple explanations of H_2-metal permeabilities which vary with membrane thickness l or with ingoing pressure p_1 between l^0 to l^{-1} and p^0 to p^1 (where 0, -1, 1, are exponents) as well as providing an explanation of the 'threshold pressure' effect sometimes observed in permeation studies, The number of limiting possibilities is large, but the theory seems ready for quantitative application, and phenomena so far recorded in the study of hydrogen flow through metals appear to be within its compass.

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