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Gaseous diffusion in porous media Part 1. - A non-steady state method

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Gaseous diffusion in porous media
Part 1.—A non-steady state method

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Abstract

Laboratory equipment, capable of modification for use on soils in the field, was constructed to study diffusion in porous systems. A simple katharometer employs the exposed element of a thermal milliammeter to measure the instantaneous composition of hydrogen/air mixtures; the most convenient working condition is when 15 mW are dissipated in the hot wire, at which the thermocouple output changes from 0·5 mV in pure hydrogen to 2·5 mV in air. The geometry of the experimental system is simple enough to permit a standard solution of the non-steady state equation for interdiffusion of two gases to be applied, and, as a check on performance, straight tubes of slightly varying geometry were used to measure the diffusion coefficient of hydrogen into air, and its dependence on temperature. Reproducibility was very good and, within the limits of experimental error, the coefficient obtained was the same for 100% hydrogen into 100% air, and 60% air + 40% hydrogen into 100% air. Measurements at 12, 20, 28 and 36° C, fitted $D = D_0(T/273)^n$, with

$$D_0 = 0\cdot651 \ cm^2 \ s^{-1} \ at \ n.t.p.$$
$$n \ = 1\cdot715$$

Standard values in the literature are $D_0 = 0\cdot611$ (International Critical Tables[11]), $0\cdot634$ and $0\cdot661$ (Smithsonian Physical Tables[13]). The latter reference gives $n = 1\cdot75$.

Introduction

IN previous laboratory studies of gaseous diffusion through porous media, some methods were unsuited to the rapid handling of numerous samples and others introduced errors affecting the validity of the results. In steady state methods, Buckingham[1] maintained a partial pressure gradient of carbon dioxide across the sample. Penman[2] measured the rate at which carbon disulphide and acetone vapours diffused through the sample and[3] improved upon Buckingham's method for carbon dioxide. Van Bavel[4] introduced refinements to Penman's vapour method. Non-steady state methods were used by Taylor,[5] in which nitrogen was the diffusing gas; by Rust and others[6] in which carbon dioxide and its radioactive isotope $^{14}CO_2$ interdiffused; and by Dye and Dallavalle,[7] in which nitrogen and carbon dioxide interdiffused. These methods produced only a very general agreement which will be considered in more detail later. One of the main difficulties in transient methods is to measure rapidly changing gas compositions without interfering with the system. Strehlow[8] used a hot-wire technique to measure the point concentration in binary mixtures in a Loschmidt cell, but found convection around the wire introduced errors in a system where all gas movement ought to be by diffusion. The present method also uses a point-analysis technique, but convection effects can be ignored because the surrounding gas approximates to a well-stirred mixture.

Measurement of gaseous composition

In thermal conductivity gas analysers, the temperature of the sensitive element is usually deduced from its instantaneous resistance, whereas the present apparatus measures the potential difference across an attached thermocouple. The sensitive element is a modified Vacuo-Junction tube (manufactured by Best Products Ltd.), consisting of a 5 mm length of electrically heated wire with a chromel-constantan thermocouple sealed by an insulating compound to its mid-point, the diameter of the seal being about 0·2 mm. As manufactured, this unit is enclosed in an evacuated glass envelope, but a modified form was supplied mounted in an open-ended glass tube, approximately 1·3 mm in diameter, with the element inset about 6 mm from the open end. In a later modification, the whole of the protective glass sheath was removed.

The output of the thermocouple for a range of heating currents was measured on a portable potentiometer reading to 1 μV, and Fig. 1 shows the response in atmospheres of hydrogen, air and carbon dioxide. There is an upper limit to the useful sensitivity, governed by the lowest power dis-
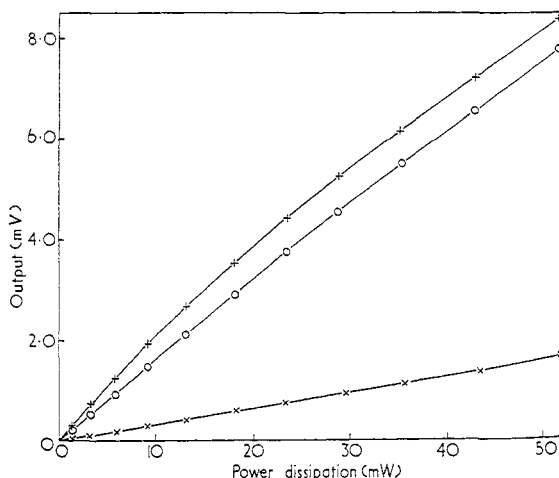

Fig. 1. Power dissipation and thermocouple response in hydrogen, air and carbon dioxide

$\times$ = hydrogen;　$\circ$ = air;　$+$ = carbon dioxide

sipation at which thermal drift becomes apparent. Thermal drift occurs when the excess temperature of the element is so great that both the cold junction and the surrounding gas increase slowly in temperature. An increase in cold junction temperature depresses the thermocouple output and an increase in ambient gas temperature increases the temperature of the element. Though thermal drift can be eliminated by continuously changing the sample being analysed, in the present study this was neither feasible nor desirable. When the energy dissipated was 15 mW, the sensitivity was adequate and the thermal drift of the element in air changed the thermocouple output by less than 1 μV/min. In operation, a constant current is maintained in the element by frequent adjustment of the potential difference across a series resistance. The power dissipated in the element is independent of the operations required to balance the circuit and may, for practical purposes, be regarded as constant, varying only slightly with the temperature of the wire. The small thermal capacity of the wire allows a rapid response to changes in gaseous composition of the surrounding gas.

The modified Vacuo-Junction was mounted with Araldite in the centre of a Perspex disk, which was fixed at the upper end of a cylindrical brass tube of length 1 in. and diameter 2·25 in. This assembly is referred to as the "gas tube" in succeeding paragraphs. For calibration the gas tube was closed at its lower end and provision was made for the controlled admission of gases. The gas tube was initially filled with air at atmospheric pressure. A known volume of hydrogen was injected under pressure and allowed to mix thoroughly with the air in the tube. Atmospheric pressure was then restored and the thermocouple output read. Further volumes of hydrogen were added, to give a series of air/hydrogen mixtures, the compositions of which, with respect to the original gas, are given by the expression $\{V/(V + v)\}^N$ where V and v are the volumes of the gas tube and the added gas respectively and N is the number of additions. Another series of mixtures was prepared by adding successive amounts of air to hydrogen. As a check, potentiometer readings were plotted against N for the two series and from the intersection of the two lines the value of N corresponding to 50% composition was obtained. This enabled the ratio $V/(V + v)$ to be calculated and checked against the value computed from the measured volumes. Calibration was done in a constant temperature room and, because the gas sample and associated circuits were maintained at the same temperature, the resultant thermocouple readings incorporate all the effects of any temperature coefficients of the components in the circuits. Fig. 2 shows the calibration curve obtained at 20° C. The calibration was repeated at each of the four temperatures at which diffusion measurements were made. The effect of a 1° C rise in the temperature was to decrease the thermocouple output by about 1·7 μV in air and to increase it by about 0·5 μV in hydrogen.

Measurements of diffusion

Apparatus (Fig. 3). Two circular Duralumin plates with their inner faces ground flat were bolted through their centres and were both drilled to accept cylindrical brass tubes of the same diameter. The lower plate into which the sample tube was inserted was clamped horizontally and the upper plate holding the gas tube was free to rotate between two positions, in which the two tubes were completely isolated from each other (position I) or accurately alined and interconnected (position II). Both gas and sample tubes were made to be a push fit in their recesses. When in position I, the gas tube

could be flushed out by gas admitted and discharged throug two tubes fitted in the lower plate. When rotated int position II, the gases in the gas and sample tubes coul interdiffuse.
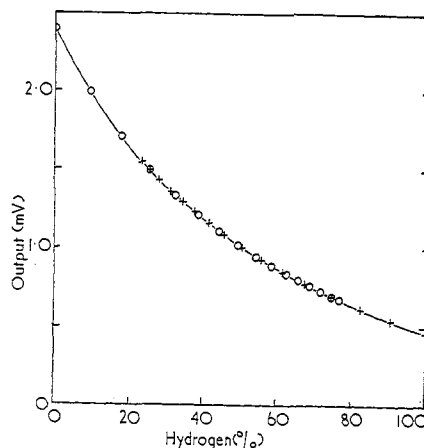

Fig. 2. Calibration curve for thermocouple in hydrogen/air mixtures at an ambient temperature of 20° C
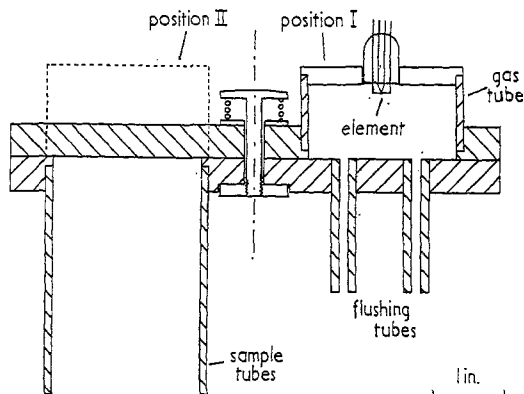$\bigcirc$ = hydrogen added to air; $+$ = air added to hydrogen

Fig. 3. Details of diffusion apparatus

In the first experiments to test the equipment, the porous material in the sample tube was a system of straight parallel tubes of known geometry. Seven Perspex tubes of nominal length 3 in. and internal diameter 0·25 in. were sealed into two circular plates of the same material, prepared so that the model could be inserted in place of the sample tube with the upper ends of the tubes either flush with the sliding plane or separated from it by the thickness of the Duralumin lip as shown in Fig. 4(*a*) and (*b*). The mean lengths and internal diameters of the tubes were measured with a travelling microscope.

Solution of diffusion equation for conditions imposed in the apparatus. Two alternative sets of boundary conditions may be imposed and a choice is needed. The first assumes that the gas in the gas tube is non-turbulent, moving only by diffusive processes so that a concentration gradient will exist between the plane containing the sensitive element and the upper end of the sample tube. Tests of the formal solution for this boundary condition on experimental data revealed consistent differences between computed and measured concentration/time curves. The second set of

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boundary conditions assumes that there is always sufficient turbulence in the gas tube to eliminate any concentration gradient in it, i.e. the contents can be described as "a well-
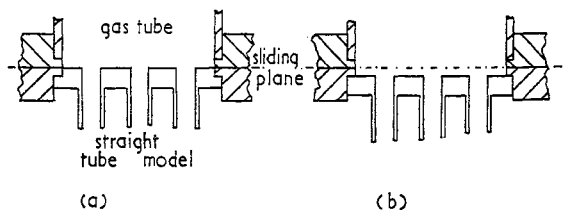

Fig. 4. The positions of the parallel tube model in relation to the sliding plane
(a) flush; (b) separate

stirred fluid". Direct and circumstantial evidence suggest that the assumption is valid. Mica dust admitted with the flushing gas and observed in a beam of light was in turbulent motion all the time until it settled out (about 5 min); and the change from position I to position II restored turbulence in a gas sample allowed to come to rest in position I. It is expected that the small heating effect of the element will maintain some degree of mixing, and a few tests showed that the response of the equipment was independent of the position of the sensing element in the gas tube. The main source of reassurance, however, is that the shapes of the concentration/time curves, and their changes with linear dimensions of the system, are in accord with expectation.

Equation of flow. Consider an element of unit area normal to the line of flow, and δx thick along the line of flow. The rate of increase of gas content is given by

$$\frac{dq}{dt} = D\frac{\partial}{\partial x}\left(\frac{\partial c}{\partial x}\right)\delta x \tag{1}$$

If the pore space is ϵ, the quantity and concentration are related by

$$q = \epsilon c\delta x \tag{2}$$

Hence the formal equation of transfer is

$$\frac{dc}{dt} = \frac{D}{\epsilon}\frac{d^2c}{dx^2} \tag{3}$$

so that D/ϵ corresponds to the thermal diffusivity in heat transfer, and the formal solution can be written down by analogy [Carslaw and Jaeger, Ref. 9, example (iv), p. 128], as follows.

Referring to Fig. 3, the open end of the sample tube, area of cross-section A, is taken as $x = 0$, and the upper end as $x = l$, where it is in contact with the gas tube of depth a. The boundary conditions are:

$t = 0$, in the region $0 < x < l$ there is zero concentration of the diffusing gas;
  in the region $l < x < l + a$ there is concentration c_0 of the diffusing gas.
$t > 0$ at $x = 0$, $c = 0$
   $0 < x < l$, $c = c$
  $l < x < l + a$, $c = $ the concentration at $x = l$, and is independent of x.

If the sample tube contains a porous material of porosity ϵ, then the instantaneous concentration in the region $0 < x < l$ is given by

$$c = \sum_{n=1}^{\infty}\frac{2hc_0\exp(-D\alpha_n^2t/\epsilon)\sin\alpha_nx}{\sin\alpha_nl\{l(\alpha_n^2 + h^2) + h\}} \tag{4}$$

where $h = \epsilon/a$, and α_n, with $n = 1, 2, \ldots$, are the positive roots of $\alpha\tan\alpha l = h$. At $x = l\delta$

$$\frac{c}{c_0} = \sum_1^{\infty}\frac{2h\exp(-D\alpha_n^2t/\epsilon)}{l(\alpha_n^2 + h^2) + h} \tag{5}$$

and for $t \gg 0$ this reduces to

$$\frac{c}{c_0} = \frac{2h\exp(-D\alpha_1^2t/\epsilon)}{l(\alpha_1^2 + h^2) + h} \tag{6}$$

A plot of $\ln c$ against t gives, after a short period, a straight line of slope $-D\alpha_1^2/\epsilon$, where α_1 depends only on the geometry of the system. As a working technique it is convenient to select from the straight part of the curve a time interval Δt such that c at t is ten times c at $t \div \Delta t$; and then

$$D/\epsilon = 2\cdot303/\alpha_1^2\Delta t \tag{7}$$

Experimental

From the calibration graph for the sensitive element, at the appropriate ambient temperature, potential differences corresponding to a series of decreasing hydrogen concentrations were read. When the gas tube in position I had been flushed with hydrogen and the potentiometer reading indicated 100% concentration, the gas tube and porous model were brought into alinement, the stopwatch started and the first of the series of voltage readings set on the potentiometer. The time at which the potentiometer circuit became instantaneously balanced was recorded. Similar time intervals were read at successive potentiometer settings corresponding to steps of $\delta\log_{10}c = -0\cdot05$. For $t > 60$ s a consistent linear relationship was obtained between $\log c$ and t, and the observations were maintained until c was about 5%. Mean ambient air temperature and pressure were observed during each diffusion measurement.

Three determinations were made at each of four temperatures for each of four systems of differing geometry. By varying the number of tubes from seven to six the value of ϵ was altered, and by fitting the model in the fully or partially recessed position, a was varied.

Ideally all samples should extend to the plane of sliding but, because the apparatus was to contain granular materials in later work, it was considered desirable to separate such samples from the carefully ground sliding surfaces by a small distance to prevent mechanical damage. Because the gas tube is in a well-stirred state, it is supposed that the hydrogen therein rapidly reaches an equilibrium concentration with the air in the gap, after which diffusion continues in accordance with the theoretical equation with a increased by the thickness of the Duralumin lip (a') so that c_0 is now $a/(a + a')$ instead of unity. The assumption appears to be justified by the close agreement between values of D_T obtained with and without the gap. (Table 1, compare columns A and B with C and D.)

Table 1. *Coefficients of diffusion of hydrogen into air in four systems of differing geometry*

$$D_T = \frac{2\cdot303}{\alpha^2\Delta t}\frac{P_0}{P} \text{ cm}^2 \text{ s}^{-1}$$

(Mean of three determinations)

Nominal temperature (°C)	A	B	System C	D	Mean
12	0·700	0·704	0·706	0·708	0·704
20	0·736	0·735	0·737	0·733	0·735
28	0·771	0·772	0·771	0·770	0·771
36	0·805	0·803	0·805	0·803	0·804

Sampling error of the mean of three samples = $\pm 0\cdot0009$

Results

The dependence of diffusion on pressure and temperature is usually expressed as

$$D_0 = D_{T,P}(273/T)^n . P_0/P \qquad (8)$$

where D_0 is the coefficient of diffusion at n.t.p.; $D_{T,P}$ is the value at T, P; n is a constant lying between $1 \cdot 5$ and $2 \cdot 0$ and expected to be close to $1 \cdot 75$ for gases and $2 \cdot 0$ for vapours [Kennard[10]].

For a system of straight parallel tubes, the porosity ϵ is simply Ae/A, where Ae is the total cross-sectional area of the parallel tubes and A is the cross-sectional area of the gas tube. Thus for parallel tubes, D/ϵ may be rewritten as $DA/Ae = D_0$, the coefficient of diffusion through free air. As a working equation, equations (7) and (8) combine to give

$$D_0 = \frac{2 \cdot 303}{\Delta t . \alpha^2} \left(\frac{273}{T}\right)^n . \frac{P_0}{P} \qquad (9)$$

Values of α were derived from the measured dimensions (Table 2) and the appropriate values of $h(=\epsilon/a)$. Values of D_T (corrected for pressure only) are in Table 1 and a linear regression of $\log D_T$ on $\log (273/T)$ gave

$$D_0 = 0 \cdot 651 \pm 0 \cdot 0003 \text{ cm}^2 \text{ s}^{-1}$$

$$n = 1 \cdot 715 \pm 0 \cdot 013$$

Table 2. *Details and dimensions of straight parallel tubes*

Model	A	B	C	D
No. of tubes	7	6	7	6
Position	Flush	Flush	Separated	Separated
a cm	2·544	2·544	2·826	2·826
l cm	7·566	7·566	7·566	7·566
Ae cm^2	0·1052	0·0902	0·1052	0·0902
A cm^2	22·099	22·099	22·099	22·099
$\alpha^2 \times 10^3$ cm^{-2}	4·940	4·294	4·492	3·902

Discussion

These small standard deviations are measures of the precision in the technique, and not necessarily measures of the accuracy of the estimates of D_0 and n. Currently quoted values for the coefficient of diffusion of hydrogen into air at 760 mm pressure and 273° K are $0 \cdot 611$,[11, 12] $0 \cdot 634$ and $0 \cdot 661$ cm^2 s^{-1},[13] and the value for n is given as $1 \cdot 75$. The value of D_0 obtained here comes within the range of the standard values of this so-called "constant", suggesting that the technique is adequate for its purpose, and that the explicit assumptions are valid. Two implicit assumptions were tested experimentally. First, as this is a transient method, the value of D_0 is an average over a range of hydrogen concentration decreasing from 100 to about 5%. Though the straightness of the plot of $\log c$ against t suggests no depen-

dence on concentration, five separate experiments were done with the initial concentration varied from 100 to 40%, but no significant variation in derived values of D_0 was detected.

Second, the possibility of an "end effect" was examined, for it may be that the effective plane of zero hydrogen concentration does not coincide with the open-end of the tube ($x = 0$). Directing a draught of air across the open end in an endeavour to make certain that $c = 0$ at $x = 0$ caused mass flow through the tubes, readily detected because the katharometer acted as a very sensitive anemometer. A much less drastic ventilation, produced by a rotary blade sweeping at intervals across the open end, caused no such mass flow: nor did it affect the rate of decay of hydrogen concentration, and it is presumed that the "end effect" is negligible and such sweeping is unnecessary.

Whatever the undetected error here may be, it will be trivial in the main bulk of the work on porous materials which will be subject to the same experimental conditions as the straight tubes. The parameter to be discussed is D/D_0 and any uncertainties in this ratio, arising from approximation in the theory, will be very small compared with the specification of the geometries of the porous systems themselves.

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