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EXPERIMENTAL STUDIES IN RELATION TO A NEW THEORETICAL DESCRIPTION OF THE PERMEATION OF DILUTE ADSORBABLE GASES THROUGH POROUS MEMBRANES

V. HAVREDAKI

Physical Chemistry Laboratory, University of Athens, Athens (Greece)

and J.H. PETROPOULOS

Physical Chemistry Laboratory, Democritos Nuclear Research Centre, Aghia Paraskevi, Athens (Greece)

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Summary

Precise data on the permeability of porous silica and alumina membranes to dilute gases are reported as a function of the nature of the gas and of temperature. It is shown that the unusual permeability behaviour previously observed only in "Vycor" porous glass at high temperatures [8—10] is a more general phenomenon. These results cannot be accounted for by conventional "surface diffusion" theory [1, 2] even qualitatively, but can be understood on the basis of recent, more advanced, theoretical treatments [3, 4, 7]. The present data provide an experimental test (not possible on the basis of previous data) of the general correlation between permeability and extent of sorption (including both the nature of the gas and temperature) predicted by the new theoretical approach, which is shown to be remarkably successful. Differences in the detailed permeability behaviour noted here, and in the previous porous glass study [8—10], are also satisfactorily accounted for in terms of differences in the mean effective pore size of the respective membranes.

Introduction

The permeability of a porous solid to a dilute (collisionless) gas in the absence of any gas—solid interaction is treated theoretically on the assumption that it differs from that of a long capillary tube only by a purely geometrical or structural factor κ_g, such that:

$$q_S l/\Delta C_g = P_g = (4\epsilon/3A)\,\kappa_g\,(8RT/\pi M)^{1/2} \qquad (1)$$

where q_S is the measured (steady state) permeation flux density, l is the thickness of the porous membrane, ΔC_g is the gas concentration difference applied across the membrane, ϵ is the porosity, A is the specific surface area (per unit volume) of the porous solid, M is the molecular weight of the gas, R is the gas constant and T is the absolute temperature, [1]. κ_g is unity for an idealised porous medium consisting of a bundle of identical circular cylindrical pores, but cannot be predicted with any certainty in the case of real porous media. Equation (1) implies that: (i) the gas concentration within the pores (per unit pore volume) is equal to the external gas concentration at equilibirum; (ii) the gas molecules are reflected at the pore walls in a perfectly diffuse manner; and (iii) the gas molecular trajectories between successive collisions with the pore walls are straight lines. The practical implication of eqn. (1) is that the quantity $P_g\sqrt{M/T}$ should be independent of the nature of the gas and T. Helium is considered to approximate to this behaviour at ordinary and high temperatures, and its sorption into the pores to an extent satisfying requirement (i) above is, in fact, the basis of the helium pycnometry of porous solids.

Gas molecules exhibiting appreciable interaction with the solid surface are sorbed into the pores in excess of the external equilibrium gas concentration. (Thus, if C is the concentration of sorbed gas per unit volume of the porous solid in equilibrium with external gas concentration C_g, the sorption or distribution coefficient $S = C/C_g$ is $\geqslant \epsilon$; where the equality sign applies to non-interacting gas, as already noted above). The permeability, P, of such gases is treated in conventional theory on the basis of the premise that the excess sorbed gas (the adsorbed gas) produces a corresponding excess permeability P_s, i.e. [1]:

$$q_S l/\Delta C_g = P = P_g + P_s \tag{2}$$

For the dilute gases considered here both S and P are independent of C_g.

The formulation of eqn. (2) was not questioned for a long time (at least in a qualitative sense), because changes in $P\sqrt{M/T}$ do indeed appear, in practice, to parallel the variation of the observed extent of sorption caused by changing either the gas or the temperature. However, eqn. (2) has served as the basis for the formulation of detailed "surface diffusion" models for the description of the permeation of dilute adsorbable gases through porous solids. In these models [1—3], the gas flowing within the pores is pictured as consisting of "gas phase" molecules behaving exactly as required by eqn. (1), on one hand, and of "surface" or "admolecules" which are considered to migrate by means of activated jumps along the pore wall surfaces, on the other hand. Clearly, such a picture is physically unsound: if there is an appreciable adsorption force field inside the pores, then all gas molecules therein must be subject to it. Theoretical treatments based on this fundamental consideration have recently been advanced [4—7]. Distinction between "gas phase" and "adsorbed" gas molecules is not necessary or appropriate in these treatments; but if such a distinction is made in a proper and consistent manner, it can be shown [3, 7] that conventional theory is in error chiefly because the concentration of "gas phase" molecules, as now calculated, fails to satisfy requirement (i) of eqn. (1) (failure to fulfill requirement (iii) is of lesser importance).

Detailed theoretical computations on model pores have shown that the predictions of the new treatment proposed by Nicholson and Petropoulos [4, 7] are consistent with eqn. (2) in the region of relatively high adsorption and/or small pore width. Outside this region, however, P can fall below P_g, i.e. $P_s < 0$; consequently eqn. (2) cannot be maintained, even in a qualitative sense. The practical consequence of this state of affairs is a reversal of the normal trend of $P\sqrt{M/T}$ with adsorption field strength or temperature described above. Experimental evidence for such a phenomenon can be found in the work of Hwang and Kammermeyer [8–10], who observed that $P\sqrt{M/T}$ for a given gas permeating through "Vycor" porous glass followed the normal downward trend with rising T, but eventually passed through a minimum and then began to increase. These data will be further considered below. Here, it suffices to point out that the above behaviour looks very unusual from the point of view of conventional theory, but finds a natural explanation, as already indicated above, in the new theoretical approach of Nicholson and Petropoulos (who, incidentally, also carefully evaluated the validity of other proposed interpretations) [3, 7]. The question which arises now is why no other observations of similar permeability behaviour have been recorded. The answer may lie in the fact that either (i) the phenomenon in question is relatively rare in real porous media (the effect of pore structure has not yet been studied theoretically; cf. also Ref. [11]), or (ii) it is easily confounded by experimental error, etc.

The results reported here are part of an investigation of the permeability of porous membranes to a series of gases (sufficiently dilute to ensure that both S and P are independent of C_g), which has been undertaken to clarify the above question and further test the theoretical Nicholson—Petropoulos models.

Experimental

Two porous membranes were prepared by compaction of silica (Degussa, Silica TK 900 of specific surface area 160 $m^2\ g^{-1}$) and alumina (Degussa, Aluminium Oxid C, of specific surface area 100 $m^2\ g^{-1}$) powders, both consisting of essentially non-porous particles.

Compaction of the powders was effected in special rigid cylindrical dies of 1 cm bore, by means of closely fitting rigid pistons, through which a nominal pressure of ~ 7000 or ~11000 atm was applied in the case of silica and alumina respectively. The powder was added to the die in five (silica) or seven (alumina) portions, in order to limit any non-uniformity of packing density [12, 13]. After compaction of the first portion of powder, two more portions were added on either side of the first and, after compressing these, the process was repeated to produce the finished porous membranes.

He, N_2, Kr, CO_2 and ethane gases of 99.95% purity were used.

The cylindrical dies containing the porous solids were designed specially for direct vacuum-tight attachment to the permeation apparatus through soft metal gaskets.

Upstream pressure (p_0) was measured by a mercury manometer (read with a cathetometer) and was maintained constant by means of a constant-pressure device. The permeate was collected in a calibrated volume of appropriate size and its pressure, p_l, was measured at suitable time intervals by means of a McLeod gauge, taking care to ensure that p_l was kept to within 0.5% of p_0. The plug holder was immersed in a thermostatic bath controlled to ± 0.2 K.

Both membranes were initially outgassed over a period of two weeks. The temperature during this period was raised gradually to 580 K, maintained at that value for about two days and then gradually reduced back to room temperature. Similar but shorter outgassing treatment was applied after a series of preliminary runs and before commencement of the final full series of permeation experiments, which were repeated three times in the case of the alumina, and four times in the case of the silica membrane.

Results and discussion

The main experimental results, together with the chief characteristics of the porous membranes, are given in Table 1.

In view of the rather narrow limits of the variation of $P\sqrt{M/T}$, special attention was paid to the method of experimentation. Temperatures significantly below room temperature were avoided to exclude any possible criticisms along the lines of Ref. [14]. Upstream pressure was varied from $p_0 \sim 20$ torr to $p_0 \sim 120$ torr (with $p_l \sim 0$) in all cases. This precaution is necessary because P may vary with p_0, if the Henry adsorption or Knudsen diffusion limits are exceeded. The permeation experiments were performed systematically on each gas in succession, each time completing runs at several values of p_0 and at temperatures 298.2 K and 348.2 K before changing the gas. The results for each full series of runs, but the first (which was for both membranes of somewhat inferior precision), are recorded under the headings (a)—(c) in Table 1. The experimental values of P showed no significant systematic dependence on p_0. This is shown in Figs. 1 and 2 for the last series of runs on the silica and alumina membrane respectively. Accordingly, the average value was used in each case for the calculation of $P\sqrt{M/T}$ in Table 1.

Table 1 shows that when the gases studied are arranged in the order of their sorbability, the value of $P\sqrt{M/T}$ tends first to decrease and then increase again. The maximum variation recorded ranges from ~18% (for alumina at 298.2 K) to ~4% (for silica at 348.3 K) and appears clearly to be outside experimental error even in the latter case (although some anomaly in the regular trend may be noted here). A small systematic shift in the absolute $P\sqrt{M/T}$ values obtained in successive series of measurements is evident in all cases and is, no doubt, attributable to minor structural

TABLE 1

Experimental results for silica and alumina porous membranes
(P in cm^2 sec^{-1} × 10^{-3}; L in min; T in K)

		$T = 298.2$ $P\sqrt{M/T}$			L	S	$T = 348.2$ $P\sqrt{M/T}$			L	S
Membrane		(a)	(b)	(c)			(a)	(b)	(c)		
SiO_2	He	1.23_5	1.22_9	1.22_0	—	(0.4_0)	1.26_7	1.25	1.23_9	—	(0.4_0)
$l = 1.51$ cm	N_2	1.19_5	1.17_8	1.17_3	0.8_1	0.4_9	1.20_7	1.19_2	1.19_5	0.7_1	0.4_7
$\epsilon = 0.40$	Kr	1.21_3	1.20_2	1.19_7	2.1	0.7_6	1.23_0	1.20_8	1.20_5	1.6	0.62
$2\epsilon/A \simeq 4$ nm	C_2H_6	1.23_5	1.22_4	1.22_2	3.6	2.2	1.20_9	1.19_3	1.19_2	1.5	0.99
	CO_2	1.26_8	1.25_8	1.24_3	7.3	3.7	1.22_1	1.21_1	1.20_5	2.5	1.32
Al_2O_3	He	1.04_3	1.04_5		0.5_5	0.3_3	1.04_2	1.05_7		0.5_0	0.3_2
$l = 2.35$ cm	N_2	0.98_8	1.00_8		2.9	0.63	0.99_5	1.01_5		2.5	0.58
$\epsilon = 0.43$	Kr	1.02_3	1.03_8		7.9	1.01	1.01_6	1.03_0		5.2	0.71
$2\epsilon/A \simeq 5$ nm	C_2H_6	1.17_6	1.19_4		17.2	4.21	1.10_5	1.10_2		7.8	1.90

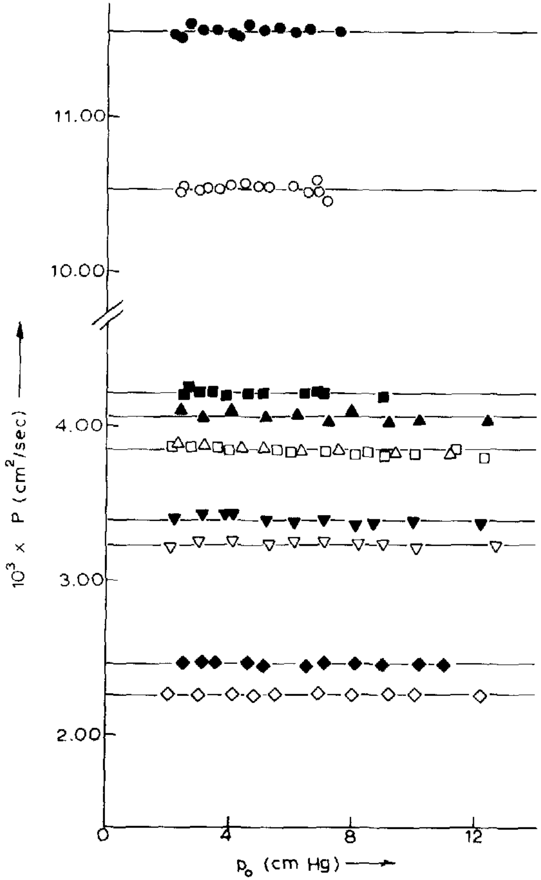

Fig. 1. Permeability of silica membrane to He (○), N_2 (□), Kr (◇), C_2H_6 (△) and CO_2 (▽) at 298.2 K (open symbols) and 348.2 K (filled symbols), as a function of upstream pressure p_0.

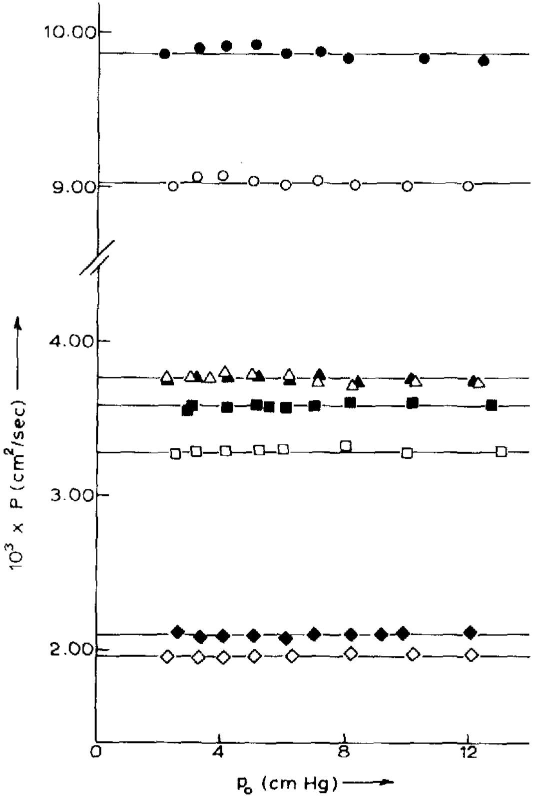

Fig. 2. Permeability of alumina membrane to He, N_2, Kr, C_2H_6 and CO_2 at 298.2 K and 348.2 K, as function of upstream pressure p_0 (symbols as in Fig. 1).

changes, or (more probably) to changes in the condition of the solid surface, in both porous solids. However, the pattern of the variation of $P\sqrt{M/T}$ with the gas within each series, remains very consistent in all cases (including the anomaly in the regular trend already noted for the silica plug at 348.2 K), which is the fundamental point of importance here.

The fact that the behaviour noted above parallels that found in "Vycor" porous glass [8] at high temperature is illustrated by the sample of the latter data given in the upper row of Table 2 (the "normal" behaviour exhibited by the corresponding ordinary temperature data is shown in the lower row of Table 2 for comparison). Some of the gases studied in Ref. [8] have been omitted from Table 2, because of some uncertainty as to the exact order of sorbability, which was not measured in Ref. [8].

TABLE 2

Examples of $P\sqrt{M/T}$ data from Ref. [8]

(P in cm^2 sec^{-1} × 10^{-4}; T in K)

T	He	Ne	N_2	CO_2
585	1.447	1.424	1.396	1.455
273.2	1.334	1.339	1.442	2.418

In the present work the relative extent of sorption was determined through the corresponding permeation time lags, L. It is well known that for a membrane–penetrant system obeying Henry's and Fick's laws (S, P = const.),

$$L = l^2 S/6P \tag{3}$$

There will be deviations from this simple relation if S and P happen to be functions of concentration or of position in the membrane (non-homogeneous medium) [15]. The time lags for both porous membranes were not found to exhibit any significant systematic dependence on p_0 within the limits of experimental error. Experimental error was considerable in the case of the least sorbable gases and L for He in the silica membrane was not measurable with any certainty. On the other hand, L for CO_2 in the alumina membrane turned out to be inconveniently long and further work with this system was abandoned. The values of L listed in Table 1 and used to calculate S by means of eqn. (3) refer to the last series of permeation runs for each membrane. The values of S must be considered as relative, rather than absolute, measures of the extent of sorption (because of the possible deviation from eqn. (3), referred to above, as a result of any inhomogeneity of the density of compaction in the relevant porous solids). This is quite sufficient for present purposes and enables us to carry analysis of our results considerably further than is possible with the data of Ref. [8].

In the treatment of Nicholson and Petropoulos [7], the adsorbability of the gas is measured by U_0, the maximum depth of the adsorption potential energy well for the gas molecule on a structureless solid surface. It is shown that, for a model pore of given effective width, $P\sqrt{M/T}$ (which differs only by a constant from the parameter $\phi = P/P_g$ used in Ref. [7]) can be described as a unique function of U_0/kT, which generally exhibits a minimum. This leads us to expect here a general correlation of the same general form between $P\sqrt{M/T}$ and S. Figure 3 shows that this holds fairly well for the silica membrane and remarkably well for the alumina one (cf. Figs. 2 and 3 in Ref. [7]; one should, of course, bear in mind that a change of gas here affects not only U_0, but also the effective pore radius, in the model of Ref. [7]; however, the latter effect is a relatively minor one).

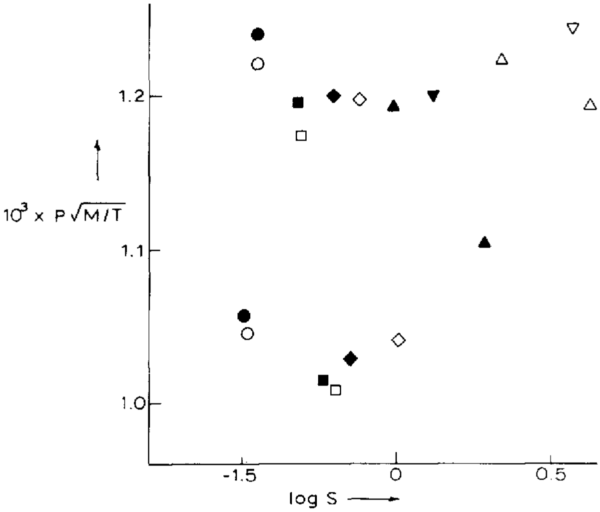

Fig. 3. Correlation between $P\sqrt{M/T}$ (P in cm^2 sec^{-1}; T in K) and S in silica (upper plot) and alumina (lower plot) porous membranes at 298.2 K (open symbols) and 348.2 K (filled symbols): He (○), N_2 (□), Kr (◇), C_2H_6 (△), CO_2 (▽).

Another important prediction of the Nicholson—Petropoulos model is that the minimum $P\sqrt{M/T}$ value should shift to higher values of U_0/kT in wider pores. This explains why it is found here at lower temperatures than in "Vycor" porous glass (cf. lower row of Table 2). In fact, the mean (cylindrical) effective pore radius $r_e = 2\epsilon/A$ of the membranes studied here (see Table 1) is considerably larger than that of "Vycor" ($r_e \approx 2$ nm) [8].

Conclusion

The analysis of the present results given above enables us to answer the question raised in the introductory section. It is quite clear that the behaviour of $P\sqrt{M/T}$ observed here is similar to that exhibited by "Vycor" porous glass at higher temperatures [8—10]. Hence the phenomenon appears to be a general one, as predicted by the theoretical models of Nicholson and Petropoulos [3, 4, 7].

Determination of the relative extent of sorption of the gases studied at the temperatures used has enabled us to carry analysis of the present results considerably further than is possible with the data of Ref. [8—10]. In the light of this analysis and bearing in mind the heterogeneity of real surfaces and the complex and variable structure and geometry of real pores, the model of Ref. [4, 7] (based on single idealised pores and homogeneous structureless solid surfaces, but using an otherwise self-consistent and rigorous treatment) has proved remarkably successful. This model also successfully explains the difference in the detailed $P\sqrt{M/T}$ behaviour between "Vycor" porous glass and the silica and alumina membranes studied here in terms of their different mean effective pore size.

In contrast to the success of the Nicholson—Petropoulos approach demonstrated above, the inability of the conventional "surface diffusion" theory to explain the dilute gas permeability behaviour found here is, of course, obvious.

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