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THERMOGRAVIMETRIC DETERMINATIONS OF THE WATER SORPTION CHARACTERISTICS OF MOLECULAR SIEVE IN HIGH-PRESSURE CO_2 AND N_2

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ABSTRACT

The rates and extents of H_2O adsorption by molecular sieves have been determined in order to assess the possibility of using these materials as desiccants in the driers on advanced gas cooled nuclear reactors. Microbalance experiments have been conducted on AW500 and 3A sieves at a sorption temperature of 35°C, using N_2 and CO_2 as carrier gases and at total pressures between 2 and 43 atm. Interpretation of the microbalance data is complicated by co-adsorption of carrier gas and water. The large differences in adsorption and desorption rates between the carrier gas and water (due to very large concentration driving forces for the mass transfer processes) allow quantification of the adsorption of both components using weight data only.

INTRODUCTION

The coolant gas in an advanced gas cooled reactor (AGR) is primarily CO_2 although other gases, such as water vapour, are present in small amounts. Control of the moisture content is currently achieved by the use of driers filled with beads of silica gel. The moisture capacity of this desiccant is higher in air than under the 40 atm CO_2 pressure experienced in AGRs, indicating co-adsorption of the CO_2 [1]. The work reported here is part of a study initiated in order to ascertain whether molecular sieves had any potential for replacing the existing desiccant and involved the determination of the relevant sorption capacities and kinetics.

A thermogravimetric technique was used since it was more rapid than methods exploiting packed beds or similar systems. In addition, by careful calibration, etc., it proved possible to determine the magnitude of the co-adsorption problem, i.e., the reduction of water capacity due to adsorption of CO_2.

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EXPERIMENTAL

Apparatus

The apparatus is shown in Fig. 1. It consists of a Sartorious ultramicrobalance capable of operating at the desired pressures (up to 45 atm) and an arrangement for controlling the flow and composition of gas passing over the reacting particles. Molecular sieve pellets were suspended in a quartz tray from one arm of the balance and the weight change monitored as a function of time as water vapour was adsorbed. Usually about six 1/16-in. pellets were used in order to produce a sufficiently large total weight change, although one 1/8-in. particle was found to be adequate. The pellets were cylindrical in cross-section and were truncated before reaction into a right-cylindrical shape. This process aids the interpretation of the data since the kinetic expressions describing diffusion in such systems are identical in form to those for a sphere. The mode of operation of the apparatus was as follows.

Carrier gas (CO_2 or N_2) was led from a cylinder into two desiccant beds (B1 and B2 in Fig. 1) containing high and low moisture loadings, respectively. Variations in the relative flows through these beds produced the desired water vapour concentration in the reaction gas. A supply of dry gas was taken from the outlet of the bed of regenerated desiccant (B2) and passed into the microbalance, the flows through each of the two arms of the balance being adjusted to the values required during the experiment. This procedure enabled the system to stabilise in dry gas at the correct reaction temperature (35°C) in order to determine an accurate initial weight reading and also to balance any aerodynamic effects of high flow rates. The temperature of the gas flowing past the pellets was adjusted to the desired

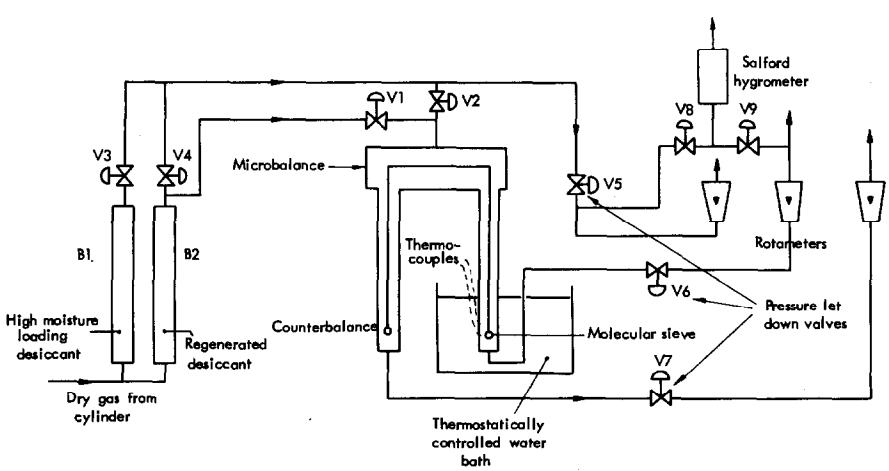

Fig. 1. Apparatus.

value by means of a thermostatically controlled water bath containing the lower parts of both balance arms.

The flows of gas through V3 and V4 were adjusted until the gas mixture contained the required H_2O vapour concentration and the overall flow through V5 equalled the total flow of dry gas entering the microbalance via V1. On achieving stable conditions, V1 and V5 were closed and V2 opened allowing wet gas into the system at the correct rate. V5 was closed to ensure the correct gas flow rate through the microbalance.

The concentration of H_2O in the gas entering and leaving the balance could be determined by passing a small flow (100 cm^3 min^{-1}) from the main flow through a Salford hygrometer. A continuous record of $[H_2O]$ could therefore be obtained throughout the experiment. It was observed that, once set, the valves V3, V4 rarely required adjustment and, provided that the ambient temperature remained fairly constant, the amount of water vapour in the reactant gas did not vary much. Experiments were left running overnight, $[H_2O]$ not deviating by more than $\pm 10\%$ during that period.

Regeneration of the molecular sieve was carried out in the microbalance at 40 atm, with a flow of carrier gas containing 300 vpm H_2O passing over the pellets. The balance arm was heated by means of a vertical tube furnace and the system temperature allowed to rise slowly up to either 200 or 280°C. This temperature was maintained until there was no further change in the weight of the particles or in the water content of the gas flowing out of the balance. The apparatus was then filled with dry gas and simultaneously cooled down to the reaction temperature of 35°C.

Microbalance operation at high pressures

Baseline characteristics of the microbalance are affected by experimental variables such as gas flow rate. Aerodynamic forces exert a drag on the particles and sampling basket in the measurement arm as well as on the counterbalance weights. Adjustment of the gas flows during operation balances the drag on each arm, so that the apparent weight of the particle is identical under static and flowing conditions. Provided that the experiment is conducted isothermally. no correction to the measured weight change is necessary. As the pressure in the system is increased, aerodynamic effects become less important since, at constant mass throughput, the velocity of the reaction gas is inversely proportional to gas pressure.

As the density of the gas surrounding the reacting material increases due to rising pressure, complications due to buoyancy become significant. Because of the small, inevitable, difference in volume between the two balance arms (denoted ΔV) there is a change of weight ΔW_P given by

$$\Delta W_P = \Delta V \Delta \rho_P \qquad (1)$$

where $\Delta\rho_P$ is the change in gas density caused by the pressure variation. Figure 2 shows plots of the baseline against pressure for two empty quartz baskets of different size, both suspended in the measurement balance arm, the counterbalance and suspension wires being the same for both cases. It is evident firstly, that in one case ΔV is negative and in the other positive, and secondly, that weighing in CO_2 produces greater baseline shifts than weighing in N_2. Equation (1) shows that the ratio of the slopes of the plots for a basket suspended in air and CO_2 is proportional to the relative densities of these two gases, or more simply to the ratio of their molecular weights. This is found to be the case for both examples shown in Fig. 2. In addition, the difference in volume between the two baskets tested should be given by the expression

$$\left[\frac{\Delta W_P}{\Delta\rho_P}\right]_1 - \left[\frac{\Delta W_P}{\Delta\rho_P}\right]_2 = (V_1 - V_2) \tag{2}$$

where V_1 and V_2 are the volumes of the two pieces of quartz. The validity of eqn. (2) may be verified by calculating the term $(V_1 - V_2)$ through the weight difference and the known density of quartz glass, this being found to be 0.0670 cm^3 compared with a value of 0.0657 cm^3 from eqn. (2).

Because of the effects of buoyancy, a correction has to be applied to all measurements made on the microbalance at high pressure. The true weight change (W) due to hydration/adsorption is related to the measured one

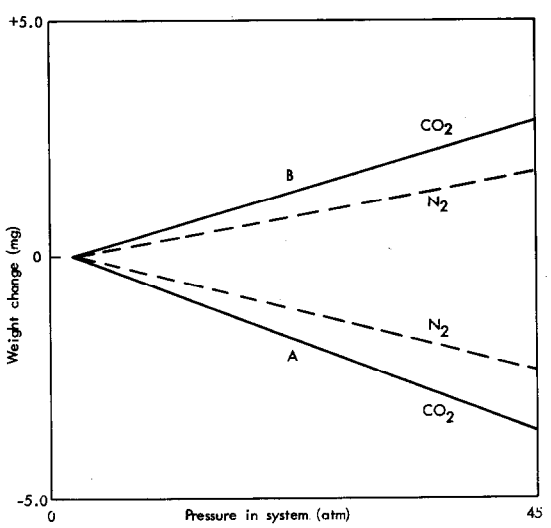

Fig. 2. Plots of baseline weight as a function of total pressure for two empty quartz baskets (A, B) weighed in CO_2 and N_2.

(W^*) by the expression

$$W = W^*\left(1 + \frac{\rho_g}{\rho_m}\right) \tag{3}$$

where ρ_g and ρ_m are the densities of the gas and particle, respectively, at the operational conditions of pressure and temperature. For the case of molecular sieve reacting at 35°C in 40 atm CO_2, the correction is not very significant, W/W^* being about 1.06.

Raising the temperature of the system also produces a significant effect on the baseline of the microbalance. During regeneration of the molecular sieve, the furnace is placed around one side of the balance so the apparatus responds to changes in density in the measurement arm compared with the counterbalance arm. By analogy with eqn. (1)

$$\Delta W_T = \Delta V_T \Delta \rho_T \tag{4}$$

where ΔV_T is the volume of the heated arm and $\Delta \rho_T$ is the density change caused by the temperature variation. Since the density is reduced on increasing the temperature (proportional to T^{-1}), it would be expected that raising the temperature would cause an increase in baseline weight. This was confirmed by experiments which showed that when six unhydrated pellets were subjected to a temperature rise from 35 to 280°C, a baseline weight change of around 6 mg could be detected. This is considerably more than the weight change resulting from the hydration, and it was therefore considered that any measurements of regeneration kinetics would be subject to large experimental errors.

RESULTS

Adsorption of carrier gas

The value of the microbalance in determining the rate of reaction as well as the ultimate hydration capacity of a molecular sieve particle depends largely on the attribution of an observed weight change to a single process. Consideration of the data presented here indicates that the hydration of the desiccant was accompanied by desorption of the carrier gas so that measured weight changes were inevitably lower than would otherwise be the case. An example of this is the hydration of 1/16-in. AW500 pellets (at 40 atm pressure, 35°C and with 300 vpm H_2O), results being shown in Fig. 3. A significant weight change was obtained when an N_2 carrier gas was used, although with CO_2 only a small increase could be detected. In fact, it was noticed that there was an initial decrease in weight in the case of CO_2, suggesting that adsorption of H_2O displaced CO_2 from sites on the molecular sieve. The overall change in weight at the end of the 20-h experiment was

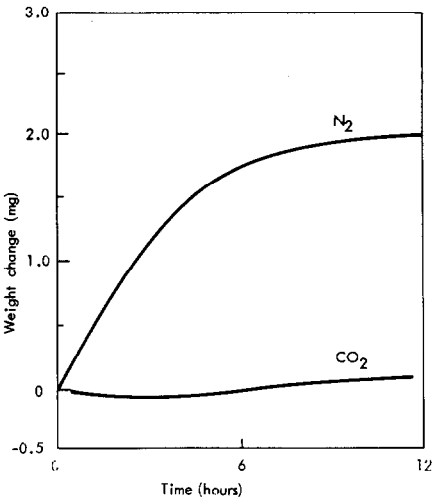

Fig. 3. Plots of measured weight change as a function of time for six 1/16-in. AW500 pellets reacted in 300 vpm H_2O at 35°C in 40 atm N_2 or CO_2.

minimal and hence estimates of the water capacity impossible. In order to confirm that the particles had in fact absorbed H_2O, the gas stream emerging from the microbalance after passing over the particles was monitored during regeneration at 40 atm CO_2, 300 vpm H_2O, a temperature of

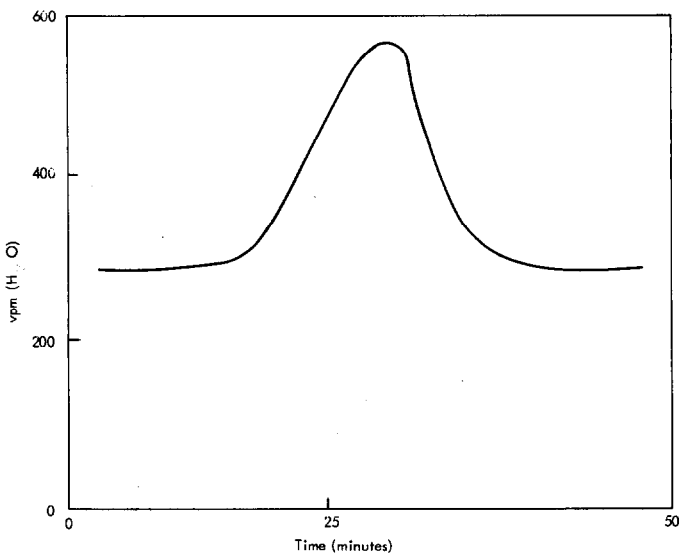

Fig. 4. Plot of water concentration in exit gas stream during regeneration of AW500 pellets in 300 vpm H_2O, 40 atm CO_2.

200°C being finally attained. Figure 4 shows a trace of the H_2O concentration against time during this heating period; the particles being regenerated are those which showed no weight change in CO_2. A significant quantity of water was driven off the sieve during heating, integration of the curve of Fig. 4, together with knowledge of overall gas flow rates, indicating that 1.96 mg was evolved. Even after allowing for errors in the determination, such as desorption of water from the stainless-steel pipework, it may be concluded that AW500 molecular sieve reacted with H_2O vapour in CO_2 does absorb water but that displacement of CO_2 also occurs. Coincidentally, it appears that under these particular conditions the weight of water absorbed is approximately equal to the weight of CO_2 desorbed, yielding a zero overall weight change throughout the experiment.

Clearly, in order to calculate the extent of hydration from the observed weight changes, it is important to determine the extent of carrier gas desorption due to H_2O adsorption. This was achieved by studying the weight increases caused by raising the pressure in the microbalance with molecular sieve pellets suspended on the quartz tray in the carrier gas. When step changes were made in the pressure in the system, the resulting variations in baseline weight were rapid and completely reversible. (This is in complete contrast to the hydration process which, under the conditions employed here, is slow and effectively irreversible). In addition, the extent of baseline shift was found to be dependent on the dryness of the particle (i.e., before or after regeneration). Figure 5 shows typical data for the magnitude of the apparent weight changes plotted against system pressure for some 1/16-in. 3A pellets weighed in both dry CO_2 and dry N_2 before and immediately

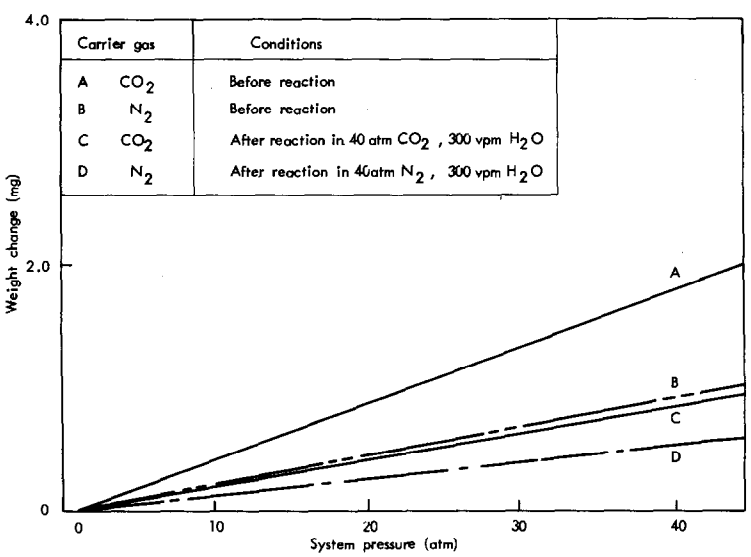

Fig. 5. Plot of weight changes for six 1/16-in. 3A pellets as a function of system pressure.

after hydration. Using the assumptions that carrier gas adsorption is rapid and reversible, whereas hydration is irreversible and relatively slow, it is possible to equate the difference in baseline weights between wet and dry pellets to the extent of carrier gas desorption during hydration. By a similar argument, it is possible to estimate the absolute magnitude of the carrier gas adsorption by comparing the change in baseline when pellets are subjected to an increase in pressure to that calculated from their known volume and the theoretical buoyancy correction using eqn. (1). It was thus possible to estimate the extent of adsorption of CO_2 and N_2 from the baseline variation as the pressure was altered and this was found to vary with the dryness of the particle (i.e., either before or after regeneration). Table 1 sets out typical fractional adsorptions of CO_2 and N_2 by AW500 and 3A molecular sieves when regenerated at 200°C and 40 atm in 300 vpm H_2O and after reaction at or around 40 atm in 300 vpm H_2O at 35°C.

In the case of AW500 sieve reacted with H_2O in CO_2, the observation that no weight change occurred even though the particle hydrated suggests that the weight of H_2O adsorbed equalled the weight of CO_2 desorbed. This in turn suggests that 1 molecule of CO_2 was displaced by nearly $2\frac{1}{2}$ molecules of H_2O on this material. From the data given in Table 1 this fact may be utilised to suggest that the hydration capacity of this material is about 9%. For 3A sieve, however, 5.7 molecules of H_2O were required to displace one CO_2, which suggests that competition for available sites is not so severe with this material as for AW500, this conclusion being compatible with the relative pore diameters of the two molecular sieves.

Equilibrium capacity of molecular sieves

The adsorption capacity of the molecular sieves under the experimental conditions of the microbalance are shown (after correction for buoyancy and co-adsorption) in Fig. 6 where the data are plotted as the equilibrium

TABLE 1

Capacities of AW500 and 3A molecular sieves for N_2, CO_2 at 40 atm, 35°C

Sieve	State	Carrier gas	Wt. carrier gas (g) per g sieve
AW500	wet	CO_2	0.10
	dry	CO_2	0.19
	wet	N_2	0.006
	dry	N_2	0.012
3A	wet	CO_2	0.006
	dry	CO_2	0.05
	wet	N_2	0
	dry	N_2	0.007

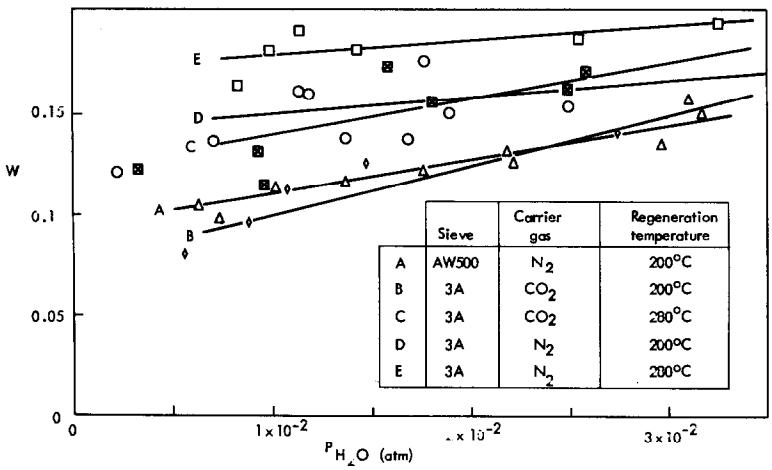

Fig. 6. Plots of measured H_2O uptake against the partial pressure of H_2O.

loading against water concentration. It is clear from this diagram that, for the majority of the results, the loading is not very sensitive to the H_2O partial pressure; i.e., the part of the isotherm under investigation is nearly flat. In consequence, the derivation of the characteristics of the isotherm is not likely to be particularly accurate. However, on the assumption that the hydration of molecular sieves under the experimental conditions follows a Langmuir isotherm, then the amount of H_2O adsorbed (W) may be described by the expression

$$\frac{W_{max}}{W} = 1 + \frac{B}{P_{H_2O}} \tag{5}$$

where W_{max} is the maximum water loading, B is a constant and P_{H_2O} the partial pressure of H_2O in the ambient gas.

For the situation under consideration here, it is impossible to completely regenerate the material by heating to 200 or 280°C in 300 vpm H_2O, and hence W_{max} represents the maximum amount of H_2O which may be adsorbed and desorbed by the sieve under the particular regeneration conditions employed. Manipulation of eqn. (5) suggests that a plot of $1/W$ against $1/P_{H_2O}$ should yield a line from which the constants W_{max} and B may be readily obtained, approximate values of these constants being tabulated in Table 2.

Kinetic analysis

The data obtained in this study have been analysed in order to ascertain the rate of water sorption and hence the diffusional parameters associated with the molecular sieve. It was assumed that the hydration kinetics were

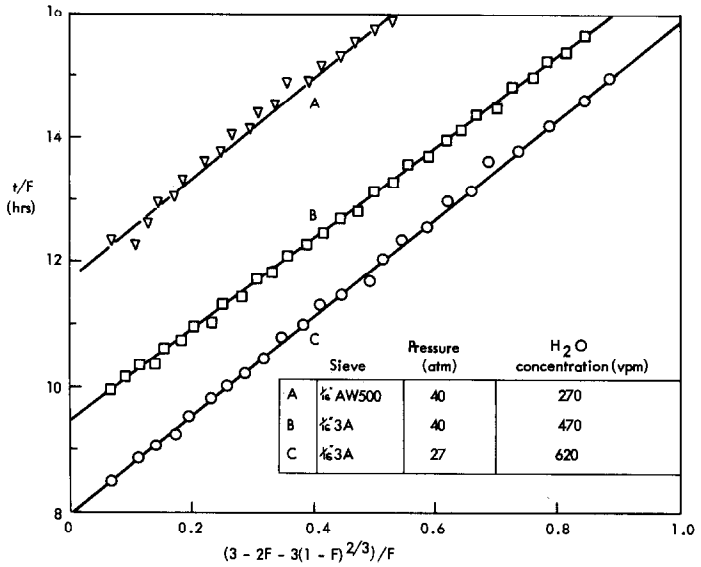

Fig. 7. Typical plots of t/F against $[3-2F-3(1-F)^{2/3}]/F$ (from eqn. 6).

controlled by two factors, the rate of mass transfer of H_2O across the solid/gas boundary layer and the rate of its diffusion into the porous particle. Using a quasi-steady state approach and the approximation of the shrinking-core model, it may be shown [2] that the rate expression may be given by

$$\frac{4\pi R^2 C_0 t}{\Delta M F} = \frac{1}{kg} + \frac{R}{2D_s F}\left[3 - 2F - 3(1-F)^{2/3}\right] \tag{6}$$

where R is the particle radius, C_0 the bulk gas H_2O concentration, ΔM the equilibrium H_2O loading, t the time, kg a mass-transfer coefficient, D_s the effective diffusion coefficient and F the fractional conversion. Figure 7

TABLE 2

Molecular sieve capacities for H_2O

Sieve	Carrier gas	Regeneration temp. (°C)	W_{max} [a]	B [a] (atm)	Capacity at 40 atm/300 vpm H_2O (g H_2O/g sieve)
AW500	N_2	200	0.17	5.2×10^{-3}	0.124
3A	N_2	200	0.18	2.0×10^{-3}	0.151
	N_2	282	0.21	1.9×10^{-3}	0.185
	CO_2	200	0.17	6.0×10^{-3}	0.116
	CO_2	282	0.20	4.5×10^{-2}	0.197

[a] W_{max} and B are constants in Langmuir adsorption isotherm (eqn. 5).

shows plots of t/F against $[3 - 2F - 3(1 - F)^{2/3}]/F$, inspection of eqn. (6) indicating that kg and D_s may be easily derived from the intercept and slope of the resulting straight line. For all the experiments conducted here, the linearity of the plots was excellent, deviations only becoming noticeable at $F > 0.85$–0.9, where errors in determining F become evident due to the slowness of the adsorption at this point. For all these data, the values of weight increase must be corrected as explained earlier to account for the effects of co-adsorption of the carrier gas and of buoyancy. These can be significant, for example, an adsorption in 300 vpm H_2O at 40 bar requires correction factors of 1.13 and 1.43 for hydration in N_2 and CO_2, respectively.

For the systems studied here, the effective diffusion coefficient (D_s) is a combination of Knudsen and bulk diffusion coefficients (D_K and D_B, respectively). Satterfield and Sherwood [3] use an approximation for D_s, i.e.

$$\frac{1}{D_s} = \frac{1}{D_B} + \frac{1}{D_K} \tag{7}$$

or (since D_B is inversely dependent on pressure)

$$\frac{1}{D_s} = \frac{1}{D_K} + P\lambda \tag{8}$$

where λ is a constant. Figure 8 shows plots of D_s^{-1} against P for all the data collected in these experiments, the intercept being related to D_K and the slope equal to λ. Discussion of the magnitudes of the relevant diffusion coefficients is unnecessary here, it is sufficient to state that they are in line with other similar determinations (e.g., Nutter and Burnett [4]) and hence that the thermogravimetric technique is capable of generating reproducible results.

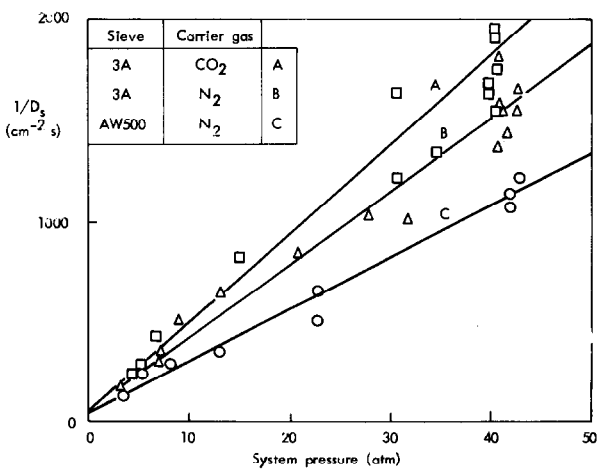

Fig. 8. Plots of reciprocal of diffusion coefficient, D, against system pressure.

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