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APPENDIX (F)

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The Concentration Dependence of Zeolitic Sorption

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ABSTRACT

The concentration dependence of sorption rates of selected gases on chabazite has been determined and interpreted in terms of the various rate controlling mechanisms present. Argon and several other gases exhibit concentration independent activated diffusion into the bulk of the zeolite. Freon 21 occupies only the pores or crevices of the mineral, and the rates are controlled by Knudsen or gaseous bulk diffusion, depending on the concentration range. Finally, carbon dioxide sorption rates strongly increase with sorbate concentrations. This probably means that at low concentrations the slow adsorption on the internal sites is the rate controlling process, while at higher concentrations the diffusion rate of the gas into the bulk of the zeolite becomes important.

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Introduction:

Sorption rates of gases on zeolites seem to depend on the sorbate concentration in various ways. Barrer and Fender determined diffusion coefficients of sorbed H_2O from D_2O - H_2O exchange rate measurements on several zeolites; (3)

(3) R. M. Barrer, B. E. F. Fender, J. Phys. Chem. Solids, 21, 12 (1961).

they noted that in the layer silicate heulandite these coefficients markedly increase with increasing H_2O concentration. H_2O causes the mineral to expand, (4)

(4) R. M. Barrer, B. E. Fender, J. Phys. Chem. Solids, 21, 1 (1961).

and this presumably leads to the increased mobility of the diffusing molecules. Thus, the situation is analogous to that encountered in swelling organic high polymers. (5)

(5) See for example, R. J. Kokes, F. A. Long, J. Am. Chem. Soc., 75, 6142 (1953); 75, 2232 (1953).

Interestingly, Barrer and Fender's data also show that the H_2O diffusion coefficients in gmelinite, a typical framework zeolite, increase somewhat with sorbate concentration. Thus, the widening of a lattice, as established for heulandite, is not necessarily the only possible reason for the observed upward trend. The situation is further complicated by the fact that in some gas-zeolite systems one finds a marked decrease of the sorption rates with increasing sorbate concentration. (6) Sometimes upward and downward trends are

(6) R. M. Barrer, D. W. Brook, Trans. Faraday Soc., 49, 1049 (1953).

found with the same zeolite if the pretreatment is varied.⁷

(7) H. W. Habgood, Can. J. Chem., 36, 1384 (1958).

It is quite conceivable that different rate controlling mechanisms are at work in the above sorption and diffusion experiments. For example, sorption rates are likely to decrease with increasing sorbate concentration if they are controlled by diffusion in and through pores or crevices, provided the concentration is too high for Knudsen diffusion,⁽⁸⁾ or if the adsorption

(8) C. N. Satterfield, T. K. Sherwood, "The Role of Diffusion in Catalysis", Addison-Wesley, Reading, Massachusetts (1963), p. 12 and 27.

on (internal) surface sites constitutes the relatively slow step. In the latter case the downward trend is due to the decrease of the number of available sites with increasing uptake.⁽⁹⁾

(9) R. M. Barrer, D. A. Ibbitson, Trans. Faraday Soc., 40, 195 (1944).

The present study is a search for this possible correlation between concentration dependence of the sorption rates and the underlying rate controlling mechanism. Earlier studies in this area^(10,11) furnish a useful basis for this

(10) W. W. Brandt, W. Rudloff, J. Phys. Chem. Solids, 25, 167 (1964).

(11) W. W. Brandt, W. Rudloff, Z. Phys. Chemie (N.F.) 42, 201 (1964).

work in that for selected gas-zeolite systems, the rate controlling steps have already been identified with some degree of certainty. For example, the sorption of argon, methane, helium, and hydrogen on a particular sample of natural chabazite was found to be diffusion rate controlled, while carbon dioxide sorption rates, especially at low temperatures, are determined by a relatively slow surface adsorption. Finally, Freon 21 was found to diffuse only into the pores, crevices, or open grain boundaries of this mineral, not into the well ordered crystalline regions. Thus, there are, for the type of systems investigated in

this laboratory, and in the temperature and concentration range covered, essentially three categories of sorption processes for which the concentration dependence of the sorption rates is to be obtained.

Experimental:

The principal sample of crystalline chabazite used in the present work was the same one described previously.^(10,11) Certain additional samples of a related nature were introduced and are discussed in the Legends to Figures (1) and (2), and Table (1).

The experimental methods employed in this work were outlined earlier.⁽¹⁰⁾ Diffusion rates, D^* , were determined as a function of the fractional amount of sorbate yet to be sorbed or desorbed in a given experiment, P^* , as described in the preceding paper of this series.⁽¹¹⁾ D^* is defined as D/a^2 where a is average radius of the grains.

The graphical comparison of the sorption rates with the solution to the diffusion equation, leading to the reported D^* values, does not imply that the processes studied are necessarily diffusion rate controlled. Instead, the discussion of the results in terms of D^* values is simply convenient and efficient since it obviates the use of numerical schemes for the evaluation of concentration dependent diffusion coefficients or of two independent rate constants if the overall rate is affected by two individual mechanisms. Moreover, the discussion in terms of D^* allows one to assess easily the relative importance of minor experimental errors.

In the earlier work, the sorbate concentration in the zeolite was permitted to change only very little during a given experiment, so that the rate curve shapes obtained would be unaffected by any concentration dependence of the rate coefficients. In the present study, the concentration again was kept nearly constant during each individual experiment, but an appreciable range of concen-

TABLE (1): Basic Experimental Data on Sorption and Desorption Experiments.

t_d , degassing time; T , experimental temperature; P_1, P_0, P_∞ , the gas pressure above the sample before at the beginning, and long time after the start of a run, respectively. s , amount sorbed; D , apparent diffusion coefficient (see text).

Run	t_d (hr's)	T (°C)	P_1	P_2	P_∞	s ($\frac{\text{moles}}{\text{g mm Hg}}$)	D ($\frac{\text{cm}^2}{\text{sec}}$)
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Sample: Chabazite grain, diameter 0.81 cm.; degassed at the experimental temperature, T .

Argon:

13/236	---	97.7	212.64	0.077	12.40	16×10^{-7}	2.9×10^{-5}
13/281	12	9.4	0	201.89	160.36	2.8×10^{-7}	1.5×10^{-6}

Methane:

13/232	15	97.8	0	27.10	23.96	1.0×10^{-7}	1.0×10^{-6}
13/234	--	97.8	76.11	0.18	13.79	2.5×10^{-7}	2.6×10^{-6}
13/259	--	50.2	93.8	1.85	24.06	7.4×10^{-7}	4.7×10^{-7}

Hydrogen:

25/28	--	99.5	184.44	1.40	3.70	--	9.2×10^{-4}
25/30	--	99.5	236.03	0.42	3.43	--	8.1×10^{-4}
25/32	--	49.1	211.2	0.52	4.29	--	5.5×10^{-4}
25/34	--	49.1	255.42	0.78	5.30	--	6.0×10^{-4}
25/39	--	3.8	211.34	409.50	403.50	3.1×10^{-8}	3.8×10^{-4}
25/40	--	3.6	403.50	249.63	253.71	3.2×10^{-8}	3.3×10^{-4}
25/41	--	3.6	253.71	10.00	16.57	7.3×10^{-8}	3.6×10^{-4}

Carbon Dioxide:

25/8	24	99.7	0	44.11	28.65	7.3×10^{-6}	2.3×10^{-6}
25/17	12	99.5	0	22.23	13.33	9.0×10^{-6}	2.3×10^{-6}
25/19	12	99.5	0	21.14	12.15	1.0×10^{-5}	2.5×10^{-6}
25/20	--	99.5	12.15	36.39	28.70	7.9×10^{-6}	4.8×10^{-6}
25/21	--	99.5	28.70	52.86	46.90	6.5×10^{-6}	5.3×10^{-6}
25/22	--	99.5	46.90	0.21	38.52	6.8×10^{-6}	3.3×10^{-6}
25/23	--	99.5	38.52	0.30	32.57	6.9×10^{-6}	3.5×10^{-5}
25/10	7	50.6	0	42.39	15.43	2.4×10^{-5}	1.1×10^{-6}
25/12	--	50.6	15.43	43.51	28.25	2.0×10^{-5}	1.2×10^{-6}
25/13	--	50.6	28.25	0.63	26.94	2.0×10^{-5}	1.8×10^{-5}
25/15	12	49.4	0	224.69	107.4	1.5×10^{-5}	1.1×10^{-6}
25/16	12	49.4	0	21.76	6.76	3.0×10^{-5}	1.1×10^{-6}
25/5	70	5.7	0	45.67	2.58	2.3×10^{-4}	1.3×10^{-6}
25/6	--	5.7	2.58	44.31	5.97	1.9×10^{-4}	1.4×10^{-6}
25/7	--	5.6	5.97	45.91	10.76	1.5×10^{-4}	1.5×10^{-6}

Freon-21:

25/64	12	13.6	0	31.3	27.9	1.2×10^{-7}	6.4×10^{-4}
25/65	--	13.6	27.9	77.3	71.9	1.3×10^{-7}	5.3×10^{-4}
25/66	--	13.6	71.9	128.0	122.0	1.2×10^{-7}	3.2×10^{-4}
25/67	--	13.6	122.0	179.4	173.8	1.2×10^{-7}	2.9×10^{-4}
25/68	--	13.6	173.8	231.3	225.0	1.2×10^{-7}	2.9×10^{-4}
25/69	--	13.6	225.0	276.6	272.9	1.2×10^{-7}	2.2×10^{-4}
25/70	--	13.6	272.9	323.9	317.4	1.3×10^{-7}	2.3×10^{-4}
25/71	--	13.6	371.4	394.6	381.8	1.4×10^{-7}	1.6×10^{-4}

25/72	--	13.6	381.8	489.5	472.1	1.5×10^{-7}	9.2×10^{-5}
25/73	--	13.6	472.1	592.6	568.7	1.7×10^{-7}	7.3×10^{-5}
25/74	--	13.6	568.7	628.1	608.3	1.9×10^{-7}	4.3×10^{-5}
25/75	--	13.6	608.3	475.4	513.8	1.5×10^{-7}	9.1×10^{-5}
25/76	--	13.6	513.8	368.9	398.8	1.2×10^{-7}	1.2×10^{-4}
25/77	--	13.6	398.8	203.3	232.2	---	3.3×10^{-4}

Sample: grain of same chabazite, average diameter 0.67 cm; degassed at above 250° C.

Methane:

13/30	12.5	50	0	27.3	24.0	4.3×10^{-7}	1.6×10^{-5}
13/32	2	50	0	15.5	13.9	3.6×10^{-7}	2.5×10^{-5}
13/33	15	50	0	26.3	23.5	3.7×10^{-7}	2.6×10^{-5}
13/34	2	50	0	28.1	25.1	3.8×10^{-7}	2.3×10^{-5}
13/35	19	50	0	108.0	95.6	4.0×10^{-7}	2.1×10^{-5}
13/36	19	50	0	110.7	97.8	4.1×10^{-7}	2.1×10^{-5}
13/37	2	50	0	108.6	95.8	4.1×10^{-7}	2.1×10^{-5}
13/38	15	50	0	110.3	97.4	4.1×10^{-7}	1.9×10^{-5}
13/39	2	50	0	201.2	177.7	4.1×10^{-7}	2.1×10^{-5}
13/40	16	50	0	113.2	99.2	4.4×10^{-7}	2.0×10^{-5}
13/41	--	50	99.2	114.1	112.4	3.9×10^{-7}	2.1×10^{-5}
13/42	--	50	112.4	130.8	128.4	3.5×10^{-7}	1.9×10^{-5}
13/43	13	50	0	112.7	98.5	4.5×10^{-7}	2.0×10^{-5}
13/44	--	50	98.5	211.2	198.6	4.2×10^{-7}	2.0×10^{-5}
13/45	--	50	198.6	307.8	296.0	4.0×10^{-7}	1.8×10^{-5}

Sample: Chabazite powder, average grain diameter 0.0088 cm.; degassed at the experimental temperature, T.

Carbon Dioxide:

13/183	19	99.2	0	13.2	1.74	5.6×10^{-6}	4.2×10^{-9}
13/184	--	99.2	1.74	13.6	4.67	3.7×10^{-6}	2.4×10^{-8}
13/185	--	99.2	4.67	14.6	7.62	3.0×10^{-6}	3.7×10^{-8}
13/186	--	99.2	7.62	16.4	10.8	2.6×10^{-6}	4.1×10^{-8}
13/187	--	99.2	10.8	17.5	13.1	2.4×10^{-6}	3.6×10^{-8}
13/188	--	99.2	13.1	18.7	15.3	2.3×10^{-6}	6.3×10^{-8}
13/189	--	99.2	15.3	10.6	11.3	3.0×10^{-6}	2.3×10^{-7}
13/190	--	99.2	11.3	7.89	8.74	3.8×10^{-6}	2.8×10^{-7}
13/191	--	99.2	8.74	5.75	6.62	4.9×10^{-6}	2.7×10^{-7}

trations was covered by series of consecutive sorption and desorption experiments.

Results:

Table (1) gives the basic results for the present series of sorption runs. The run numbers indicated in this Table allow one to correlate the present data with those reported previously; in particular, consecutive sorption steps can be identified as such.

Figure (1) shows plots of the apparent diffusion rates, D^* , against P^* , for some typical experiments. Figure (2) gives D as a function of the concentration of sorption in the sorbent at the beginning of each particular run. Some of the data included in Figure (2) are not reported elsewhere because they are of somewhat lower precision and are of use only for the comparison embodied in this Figure. The diffusion coefficient, D , for each run (Table (1) and Figure (2)) is obtained in a range of P^* where it is most nearly constant (see Figure (1) for examples).

None of the results obtained with hydrogen as a sorbate are used in Figures (1) and (2), because too little of this gas is sorbed to obtain precise values of D^* or D .

Discussion:

The results obtained for argon, methane, and hydrogen are particularly simple. For one, D^* is independent of P^* (Figure (1)), and this means that an individual rate curve is well fitted by the relevant solution to the diffusion equation.⁽¹¹⁾ Next, the initial diffusion coefficients, D , are independent of concentration over the range covered (Figure (2) and Table (1)). Thus, in agreement with the earlier work,^(10,11) the sorption of the above gases on the natural chabazite investigated here, appears to be controlled by concentration independent, activated bulk diffusion.

Next, the data obtained for Freon 21 are of considerable interest. As in the case of argon, etc., ^{the} rates conform to the solution to the diffusion equation and the sorption and desorption results agree well (Figure (1)). On the other hand, the Freon 21 rates show a distinct and negative concentration dependence, especially at the higher sorbate concentrations used (Figure (2)). Barrer and Brook⁽¹²⁾ reported sorption rates of propane and methylene chloride

(12) R. M. Barrer, D. W. Brook, Trans. Faraday Soc., 49, 1049 (1953).

on some other natural chabazite. These data, as shown in Figure (2), show very similar trends as ours, but the actual sorption rates differ greatly. Obviously, the molecular sieve effect does not account for the very high sorption rates measured for Freon 21, as compared to the ones obtained for argon or methane. It is quite likely that the Freon 21 sorption rates (Figure (2)) obtained at relatively high Freon 21 concentrations correspond to gaseous bulk diffusion in the pores or crevices of the chabazite.⁽⁸⁾ Effective diffusion coefficients of this type are known to be proportional to the sample porosity divided by the diffusion path tortuosity. At lower sorbate concentrations the Freon 21 sorption rates tend to become concentration independent, while the rates of Barrer and Brook are concentration independent over an appreciable range. It is very likely that Knudsen diffusion is important in this range; the measured rates will be proportional to the pore diameter if cylindrical pores constitute the most important defects present.⁽⁸⁾

The negative concentration dependence of Freon 21 rates also indicates that surface diffusion is probably of little or no importance in spite of the fact that the experimental temperature lies only a little above the sorbate boiling point.

The results obtained for carbon dioxide, finally, are striking in that there is a distinct increase of the apparent initial sorption rates, D^* , with concentration (Figure (2)). Obviously, the number of vacant sites yet to be filled does not control the rate of the overall process, even though there is evidence that the sorption rates are strongly dependent upon the rate of adsorption on internal sites.⁽¹⁰⁾ Interestingly, D^* at the end of a given sorption run ($P^* \rightarrow 0$) is higher than that measured at the beginning of a consecutive run. This means that the concentration dependence seen in the carbon dioxide data of Figure (2) does not, by itself, explain the observed D^*/P^* curves. It also means that the process cannot consist of a rate controlling diffusion step followed by an instantaneous immobilization of the sorbate on (internal) sorption sites, regardless whether a linear or nonlinear sorption isotherm is assumed.⁽¹³⁾

(13) J. Crank, "The Mathematics of Diffusion", Oxford University Press (1956), p. 121.

It is noteworthy that the D^*/P^* curve of the consecutive experiment referred to (see Figure (2)) lies higher and has a somewhat lower slope than that resulting from the first experiment. Also, the desorption experiments resulted in very high D^* values which were independent of P^* (Figure (1)). All this is readily understood if one assumes that consecutive sorption runs are more and more diffusion rate controlled, and that the slow surface process mentioned earlier becomes unimportant. Less and less of the carbon dioxide can be accommodated on definite sorption sites, and the rate curves (D^*/P^* of Figure (1)) are, therefore, changing.

Finally, the sorption isotherm which can be drawn from the data of Table (1) shows a very pronounced hysteresis, and the desorption proceeds more rapidly than one would expect from an extrapolation of the sorption rates (see

Figure (2)). Thus, it seems that the adsorption of carbon dioxide on the silicate sites is practically irreversible, and that a small fraction of the gas is physically sorbed only and can leave the zeolite by rapid diffusion.

The interpretation offered here seems preferable to the assumption that diffusion and irreversible adsorption are competitive or parallel mechanisms, and that the diffusion coefficient increases with increasing sorbate concentrations. This is because the nonadsorbing gases (argon, etc.) were found to have concentration independent diffusion coefficients.

In summary, the carbon dioxide results are probably due to a sequence of a diffusion and a surface adsorption process. The latter controls the sorption rates at low sorbate concentrations, while the former is evident in sorption experiments at high sorbate concentrations and especially in desorption runs. As mentioned earlier,⁽¹⁰⁾ the surface process also is relatively important at the low experimental temperatures.

It is interesting to note that the argon sorption data can be fitted better by the Elovich equation⁽¹⁴⁾ than those for carbon dioxide (Figure (3)).

(14) M. J. D. Low, Chem. Revs., 60, 267 (1960).

Obviously, this equation is too general to permit a reliable distinction of diffusion and surface control. Much literature data on heterogeneous catalytic rates may require a re-interpretation if analyzed on the basis of the Elovich equation only.

ACKNOWLEDGMENT

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LEGENDS TO FIGURES

Figure (1): Apparent Diffusion Rates, D^* , against Fractional Amount of Sorbate yet to be sorbed or desorbed in a given run, P^* . $D^* \equiv D/a^2$, where D is the diffusion coefficient, a is the (equivalent) radius of the sorbent grains. The top curve is displaced to lower values and the two bottom curves are displaced to higher values of $\log D^*$, always by one decade. The curves refer to the following runs, counting from top to bottom, along the left hand ends of the curves, giving the run numbers in parentheses: Freon-21, sorption at 13.6°C , (25/64), same, but higher concentration, (25/74). Carbon dioxide, desorption at 50.6°C , (25/13); argon, desorption at 97.7°C , (13/235)¹; argon, desorption at 97.7°C , (13/236). Argon, sorption at 50.3°C , (13/257)¹. Methane, sorption at 97.8°C , (13/231)¹; same, (13/233)¹, superposes preceding run; desorption, (13/234). Carbon dioxide, sorption at 99.7°C , (25/8); sorption at intermediate sorbate concentration at 50.6°C , (25/12); same (25/15); same, (25/10). Carbon dioxide sorption at relatively high sorbate concentration at 5.7°C , (25/7), and at lower concentration, at the same temperature, (25/5).

Figure (2): Apparent Diffusion Coefficients, D , as a Function of the Concentration of Sorbate in the Sorbent, A , at the start of each Run. Sample of chabazite, grain diameter 0.81 cm ; ³ degassing at experimental temperature:

⊙, Freon-21 sorption and desorption at 13.7°C .; ◊, methane sorptions at 100°C .; ◊, methane sorption at 50°C .; ○, carbon dioxide sorption at 100°C .; ⊙, carbon dioxide desorption at 100°C .; ⊖, carbon dioxide sorption at 5.7°C . Sample of chabazite powder, average grain diameter 0.19 cm ., degassed at 350°C .: ◊, methane sorption at 150°C .; ◊, methane sorption



















at 100° C; , carbon dioxide sorption at 150° C. Sample of small chabazite grains, average diameter 0.68 cm., degassed above 250° C: , methane sorption at 50° C. Sample of chabazite powder average grain diameter 0.0088 cm., degassed at the experimental temperature: , carbon dioxide sorption at 100° C; , carbon dioxide desorption at 100° C. Similar sample; , methane sorption at 100° C; , carbon dioxide sorption at 100° C. The experiments , , , , were obtained on equipment of somewhat lesser precision than the others. They are reported only in this Figure. The D values correspond to the maximum D* values obtained for each run (see Figure (1)). The temperatures given are approximate values. , propane sorption on chabazite at 150° C (R. M. Barrer, D. W. Brook, Ref. (6)). , methylene chloride sorption on same chabazite at 0° C (same reference).

Figure (3): Elovich Plot of Sorption Runs. P^* is the fractional amount of gas yet to be sorbed in given run; t_0 is a constant, chosen to produce the best curve fit. , carbon dioxide sorption on chabazite powder, average grain diameter 0.0088 cm., degassed at the experimental temperature, 99.5° C; , , carbon dioxide sorption on chabazite grain, 0.81 cm. diameter, at 99.5° and 5.7° C, respectively. , argon sorption on same powder, at 97.6° C; , , argon sorption on same grain, at 97.7° and 9.4° C, respectively.

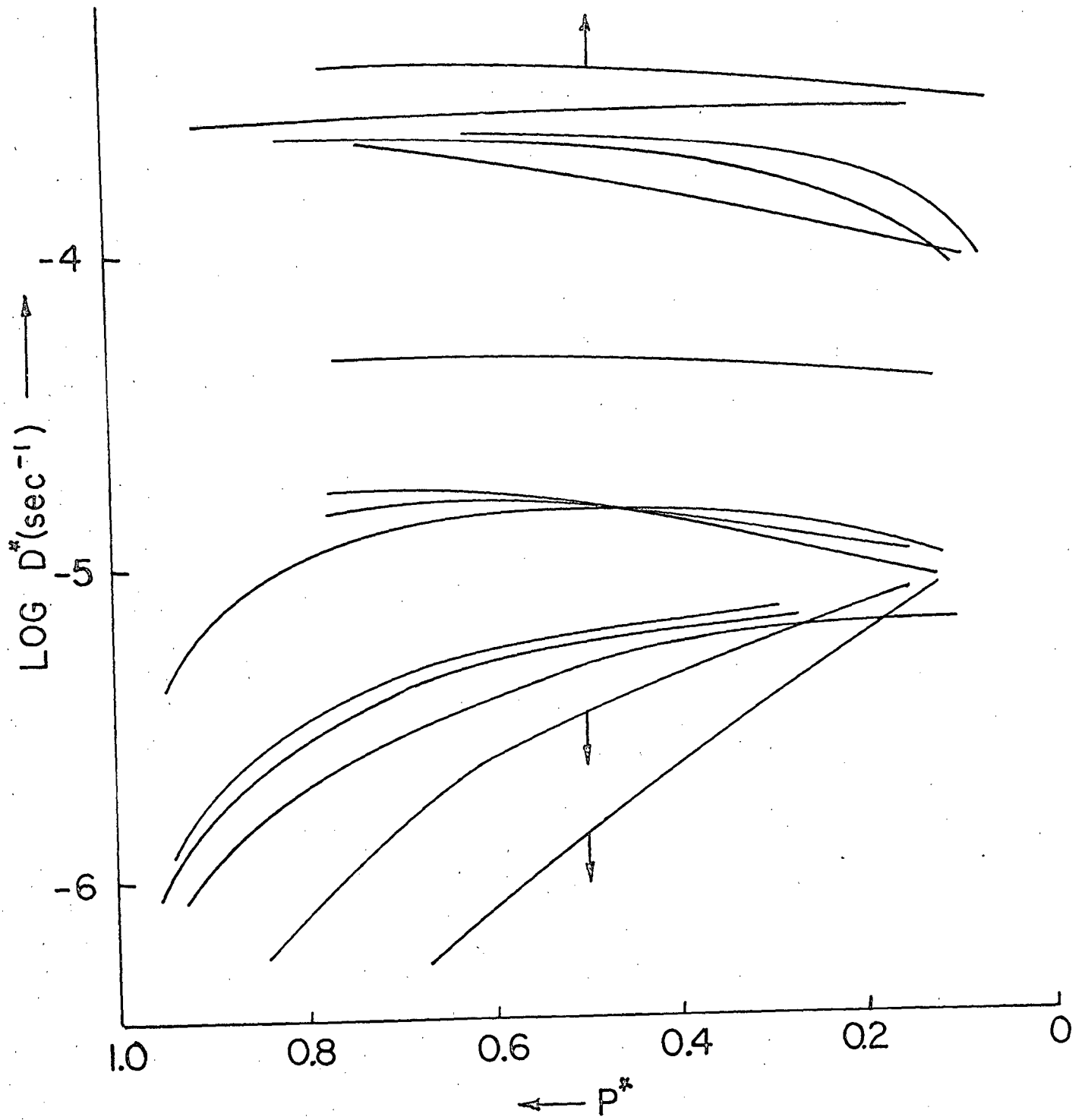


FIG. 1.

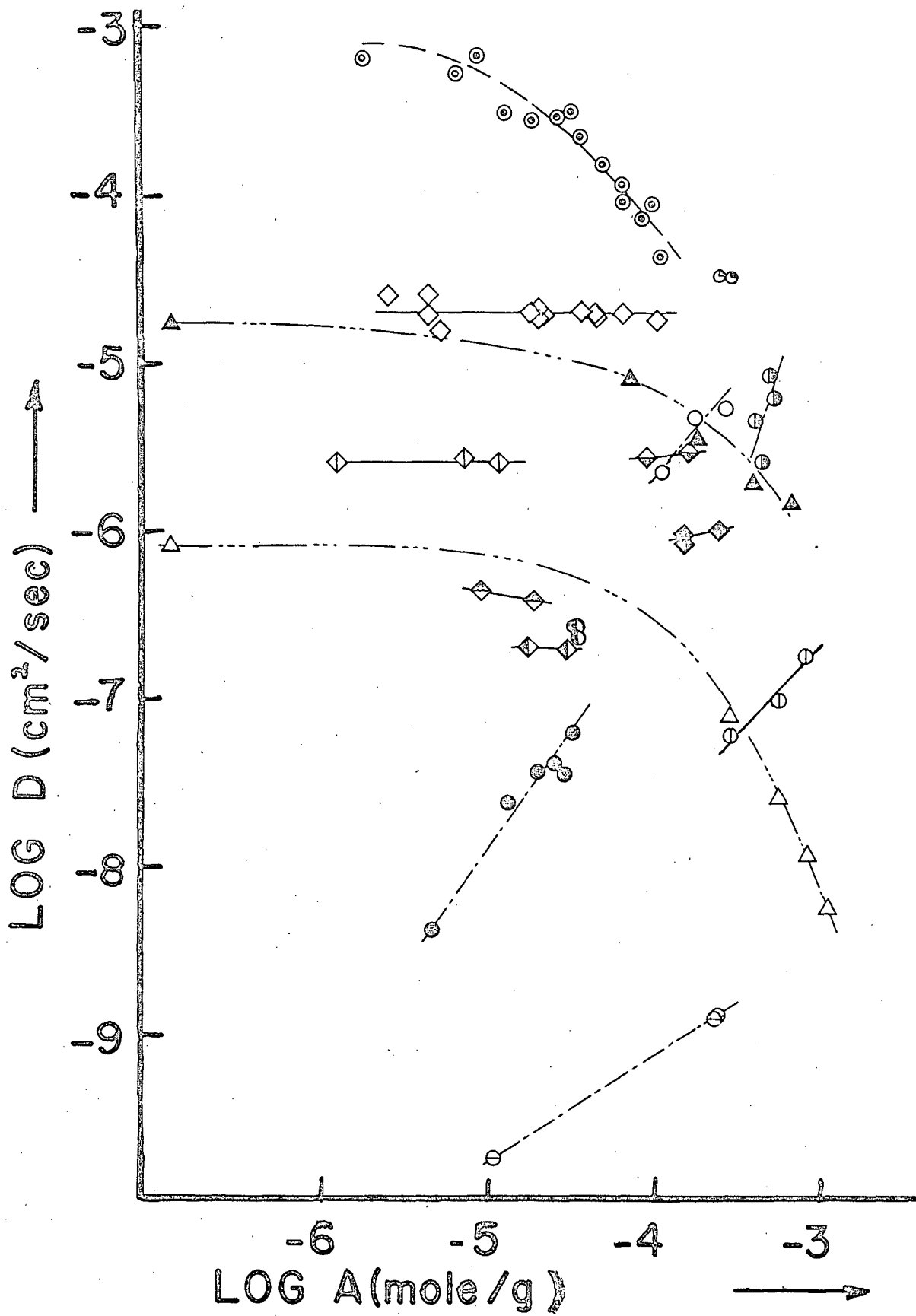


FIG. 2

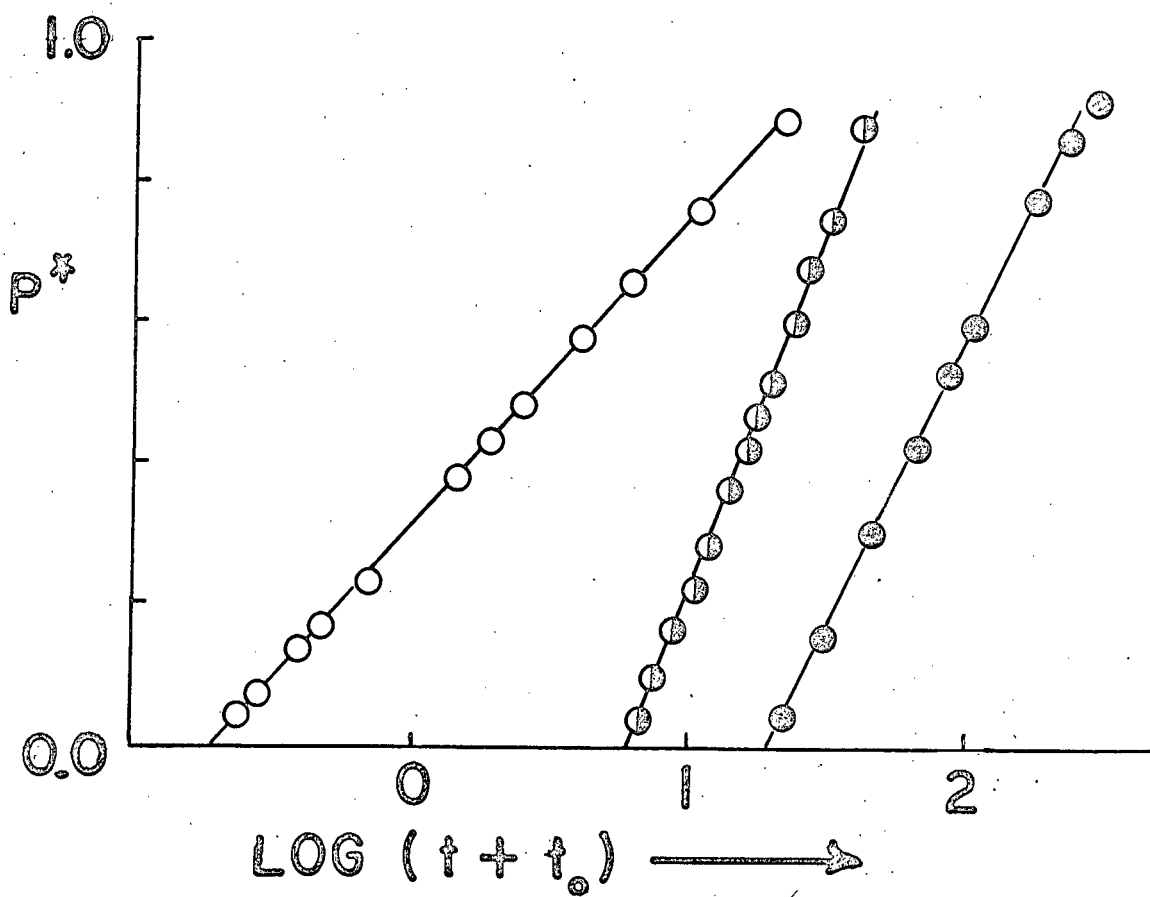
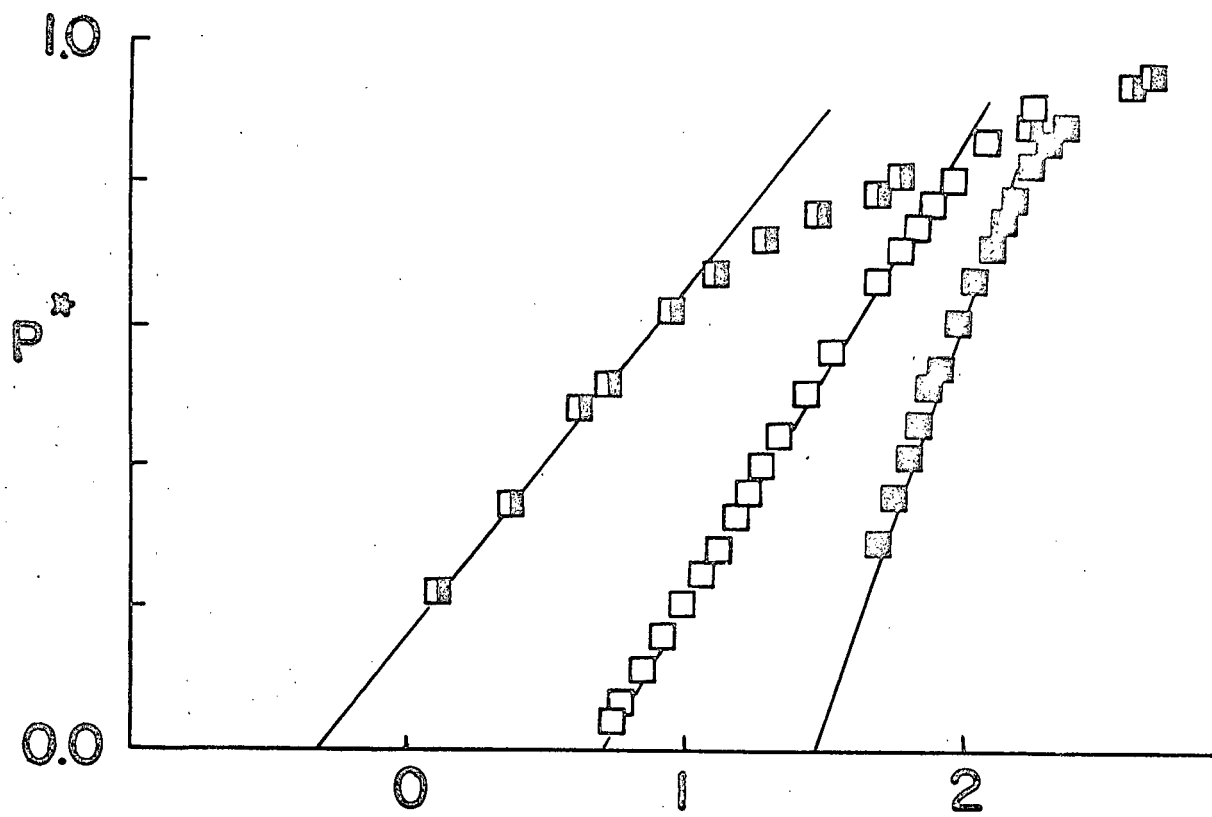


FIG. 3.