SOME TECHNIQUES FOR INVESTIGATING THE UNSTEADY-STATE MOLECULAR FLOW OF GAS THROUGH A MICROPOROUS MEDIUM*†

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An experimental method has been developed which is capable of measuring the unsteady-state molecular flow of small volumes of gas from a micro-porous solid such as are encountered under thermal conditions unfavourable to adsorption. Two new computational procedures, which do not use the severe simplifying assumptions of existing methods, are described for evaluating diffusivities from unsteady-state diffusion data. They are applied to some experimental results on the diffusion rates of several gases from synthetic zeolites.

Introduction

In recent years, applications of physical methods to fundamental coal research[1] have led to the suggestion that coals possess a somewhat unique micropore structure of the 'molecular sieve' type. In common with several previously published investigations, the major objective of the present work was to assess the validity of this 'molecular sieve' suggestion. Previous investigators[2-6] have confined their attention to diffusion measurements at temperatures below about 100°, where coal has found little commercial application and where the problem of interpretation of diffusion data is made more difficult by the presence of large concentrations of adsorbed gas. It was decided, therefore, to conduct a study at higher temperatures.

Because of possible general interest in the experimental method and computational procedures which have been employed, they are described below as a separate study. Several results have been obtained for the diffusion of some common gases through the Linde Company's Type A synthetic zeolites—a molecular sieve material of well defined structure. These results have been included in order to demonstrate the validity of the experimental and computational methods. Results on the unsteady-state diffusion of gases through anthracite will be the subject of a separate communication.

Experimental

Method

At temperatures above approximately 300°, difficulties are encountered in measuring rates of unsteady-state flow. The total volume of gas which can be loaded into the open pore structure of a given sample is small, when thermal conditions are unfavourable to adsorption. Further, the problem of temperature control frequently cannot be conveniently overcome by the use of a thermostatically controlled bath. For a system which includes a furnace operating at a high temperature, some other means of avoiding errors due to temperature fluctuations must be sought. To overcome these difficulties, a differential experimental system was selected, as shown in Fig. 1. In principle, the procedure consisted of charging the sample under investigation up to some pressure in excess of atmospheric and then measuring the unsteady-state release of gas after sudden reduction of the pressure back to atmospheric.

With the exception of the volumeter, which had a capacity of 1·5 c.c., the main section of the apparatus was constructed as symmetrically as possible. Two quartz sample tubes were used, each connected to the remainder of the apparatus by ball-and-socket joints sealed with high-vacuum wax. Each sample tube contained equal weights (∼ 20 g.) of identical samples.

The micromanometer employed was of the type described previously.[7] The measurement is based upon the movement of a bubble of air trapped in a small-bore capillary tube connecting two **U**-tube reservoirs containing a low-boiling, intermediate fluid and mercury. Since the reference pressure-side of the manometer was exposed to the same unsteady temperatures as the measuring side, it was possible to detect very small rates of gas out-flow, even in the presence of furnace temperature and room temperature fluctuations.

After the quartz tubes had been filled with samples and sealed to the apparatus, with taps S6 and S7 closed, the system was evacuated for a sufficient period of time to ensure substantially complete removal of previously charged gas. For an initial run with each sample of synthetic zeolite, the sample was outgassed for at least 24 hours at a minimum temperature of

200° to remove water. The sample tube on the right side of Fig. 1 was then exposed to the desired gas at a known pressure somewhat in excess of atmospheric through S1. The remainder of the apparatus was exposed to the same gas at atmospheric pressure through tap S3. Adequate time was then allowed for the system to attain substantially complete equilibrium.

At the start of each run, the pressure was reduced quickly to atmospheric in the right-hand tube. Then taps S3 and S4 were closed, S6, S7 and S10 were opened, and the reservoir R2 was lowered to displace the air bubble in the micromanometer from its equilibrium position. The time and volumeter readings were then noted when the bubble regained its equilibrium position, as determined by the crosswires of a cathetometer through which the position of the bubble was observed. This process was repeated throughout the run. For rapid or moderately rapid rates of diffusion, the volumeter readings were plotted against the square root of time ; and for smaller rates of diffusion, $dV_t/dt^{\frac{1}{2}}$ was plotted against $t^{\frac{1}{2}}$. The computational procedures described in the following section were then employed to evaluate the parameter $D^{\frac{1}{2}}/r_0$.

Computational procedures

Although the above experimental technique could be applied to the investigation of unsteady-state Poiseuille flow from a medium of sufficiently large particle size, it should be stressed that the computational procedures which follow are only strictly applicable to molecular flow under isothermal conditions where the rate of gas penetration may be assumed to be directly proportional to the concentration gradient. In the mathematical treatment which follows, whereas the terms 'diffusion' or 'flow' may be used with almost equal justification for activated flow (when the penetrating molecules spend most of their time within the force fields of the solid), perhaps the term 'diffusion' should not be used for non-activated molecular flow. Nevertheless, since the diffusion concept appears to have been favoured by most previous investigators, the terminology and symbolism of diffusion have been employed throughout this paper.

Fick's laws and their validity.—In recent years, a number of authors have been rather critical of the application of Fick's Second Law to the problem of gas diffusion through a solid. Babbit,[8] for example, states that the true differential equation for the diffusion of a gas in a medium can result only from a combination of the equations of continuity and of state with an expression defining the fundamental dynamic law of the system, thereby implying that Fick's
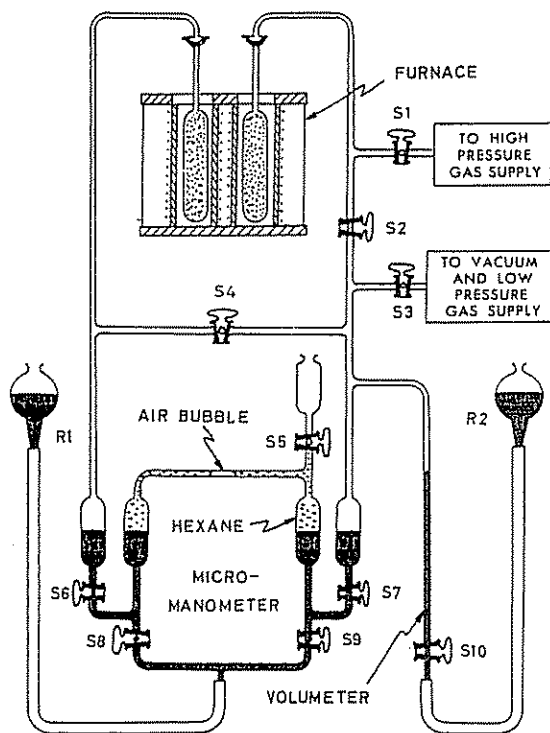

Fig. 1. *Diagram of the diffusion apparatus*

Second Law is not based upon this procedure. For moderate pressures and isothermal conditions, however, the necessity for an equation of state does not arise, if the diffusion rate at each cross-section in the medium is assumed to be proportional to the product of the concentration gradient and the diffusivity. Under these conditions, the equation of continuity for spherically symmetrical flow leads directly to Fick's Second Law in the form

$$\frac{1}{r^2} \cdot \frac{\partial}{\partial r}\left(r^2 D \frac{\partial C}{\partial r}\right) = \frac{\partial C}{\partial t} \quad \dots\dots\dots\dots\dots\dots\dots(1)$$

In spite of the fact that chemical potential (which, except for a constant factor, is the same as the potential function proposed by Babbit) appears to have been generally accepted as the correct driving force for diffusion, it has not been established experimentally that the use of this driving force leads to any improvement in the correlation of experimental data. Consequently, under the conditions stipulated above, equation (1) appears to be equally as acceptable as any of the more complex differential equations which have been proposed at the present time.

Solutions of the differential equation.—Although similar solutions are available for several non-spherical models, numerous previous investigations have shown the unsteady-state diffusion process to be remarkably insensitive to particle shape. Consequently, the radius of an equivalent sphere (r_0) may be used for most particles of irregular shape. Whereas many previous investigators have favoured an approximate solution of the type suggested by Barrer & Brook[9] which is not based upon any specific physical model, this procedure can lead to difficulties and errors in the interpretation of experimental data.

The method proposed by Barrer & Brook is based upon the solution

$$\frac{V_t - V_0}{V_e - V_0} = \frac{2A}{V}\left(\frac{Dt}{\pi}\right)^{\frac{1}{2}} \quad \dots\dots\dots\dots\dots\dots\dots(2)$$

which only applies under conditions far removed from equilibrium. Under these conditions, the time required to obtain a good estimate of $(V_e - V_0)$ is usually too large ; consequently errors are frequently introduced by substituting a value of $(V_e - V_0)$ which has been obtained by questionable indirect means. In addition, since almost any curve obtained under conditions far removed from equilibrium will appear to possess initial linearity, the method provides no estimate of the extent to which the observed variables possess a dependency of the type demanded by the theory.

In this study, the following complete solutions to equation (1) were employed to overcome the undesirable features of the approach mentioned above.

$$\frac{V_t - V_0}{V_e - V_0} = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(-\frac{Dn^2\pi^2 t}{r_0^2}\right) \quad \dots\dots\dots\dots\dots\dots\dots(3)$$

$$\frac{V_t - V_0}{V_e - V_0} = 6\left(\frac{Dt}{r_0^2}\right)^{\frac{1}{2}}\left\{\pi^{-\frac{1}{2}} + 2\sum_{n=1}^{\infty}\text{ierfc}\,\frac{nr_0}{\sqrt{Dt}}\right\} - \frac{3Dt}{r_0^2} \quad \dots\dots\dots\dots(4)$$

These solutions are well known ;[10] consequently, their derivations need not be discussed here. The series of equation (3) converges well for large values of $D^{\frac{1}{2}}t^{\frac{1}{2}}/r_0$; whereas the same solution expressed in the form of equation (4) possesses the advantage of converging rapidly for small values of $D^{\frac{1}{2}}t^{\frac{1}{2}}/r_0$.

A computation procedure for large or moderate values of $D^{\frac{1}{2}}t^{\frac{1}{2}}/r_0$.—Since three unknowns, V_0, V_e and $D^{\frac{1}{2}}/r_0$ are involved in equation (3), three equations are required which may be obtained from three points on an experimental curve—a typical example of which is given in Fig. 2. Assuming these three points to be $(V_1, t_1^{\frac{1}{2}})$, $(V_2, t_2^{\frac{1}{2}})$ and $(V_3, t_3^{\frac{1}{2}})$, the problem is to solve the following three equations simultaneously for the required unknowns

$$(V_1 - V_0) = (V_e - V_0)f_1 \dots\dots\dots\dots\dots\dots\dots(5)$$
$$(V_2 - V_0) = (V_e - V_0)f_2 \dots\dots\dots\dots\dots\dots\dots(6)$$
$$(V_3 - V_0) = (V_e - V_0)f_3 \dots\dots\dots\dots\dots\dots\dots(7)$$

where f_1 is used to denote the function

$$f_1 = 1 - \frac{6}{\pi^2} \sum_1^\infty \frac{1}{n^2} \exp\left(-\frac{Dn^2\pi^2 t_1}{r_0^2}\right)$$

Eliminating V_0 and V_c from equations (5), (6) and (7) leads to the equation

$$\frac{f_1 V_3 + f_2 V_1 + f_3 V_2}{f_1 V_2 + f_2 V_3 + f_3 V_1} = 1 \quad\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(8)$$

which must be solved for $D^{1/2}/r_0$ by a method of successive approximations. The procedure adopted was to assume values of $D^{1/2}/r_0$ successively and to converge on the required value of $D^{1/2}/r_0$ systematically. The appropriate values of V_c and V_0 were then obtained by back substitution. Although an I.B.M. 650 digital computer was used to perform this reiterative procedure, a satisfactory value of $D^{1/2}/r_0$ can be arrived at by hand calculation after three or four trials. The computer programme utilised the complete solution as given by equation (3) ; whereas for hand computation, successive values of f_1 were obtained from Fig. 3 which gives equation (3) in graphical form.

A computational procedure for small values of $D^{1/2}t^{1/2}/r_0$.—Where the experimental results produced a plot having insufficient curvature to permit application of the method described above, the following procedure may be adopted. A plot of $dV_t/dt^{1/2}$ versus $t^{1/2}$ can be prepared by measuring release rates at several minute intervals. The results can be compared with the theoretical
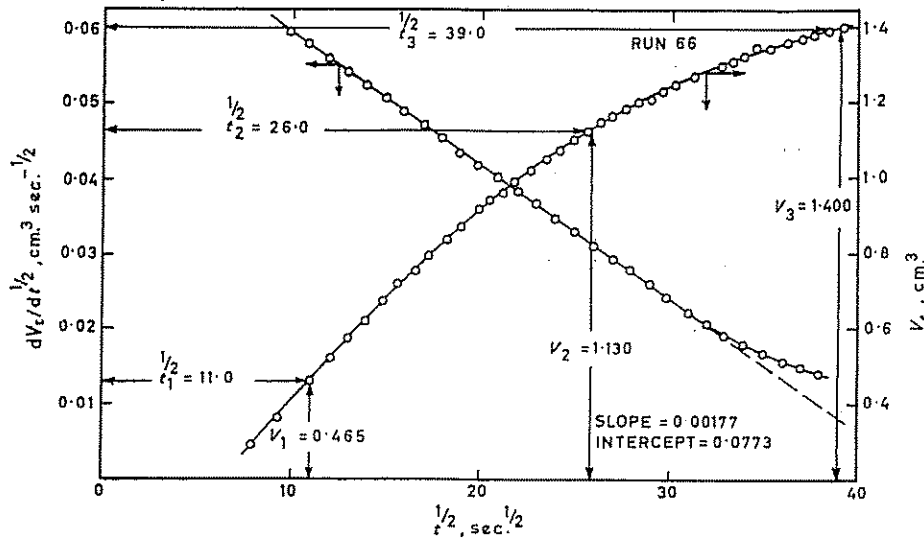

Fig. 2. *Typical set of experimental observations*
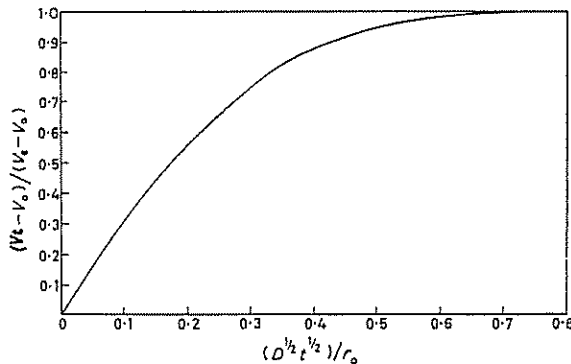(nitrogen/zeolite 3A system at 303°)

Fig. 3. *Solution to differential equation* (1)

requirements of equation (4). By differentiating equation (4) with respect to $t^{\frac{1}{2}}$, the following relationship is obtained

$$\frac{dV_t}{dt^{\frac{1}{2}}} = \frac{6D^{\frac{1}{2}}}{r_0}\left(V_e - V_0\right)\text{H}\left(\frac{D^{\frac{1}{2}}t^{\frac{1}{2}}}{r_0}\right) \quad\text{...(9)}$$

where

$$\text{H} = \left(\frac{D^{\frac{1}{2}}t^{\frac{1}{2}}}{r_0}\right) = \pi^{-\frac{1}{2}} - \frac{D^{\frac{1}{2}}t^{\frac{1}{2}}}{r_0} + \sum_{1}^{\infty}\frac{2}{\sqrt{\pi}}\exp\left[-\left(\frac{nr_0^{\pi}}{D^{\frac{1}{2}}t^{\frac{1}{2}}}\right)^2\right] \quad\text{................(10)}$$

As may be seen from Fig. 4, the terms behind the summation sign in equation (10) are insignificant up to the point X_1 where $D^{\frac{1}{2}}t^{\frac{1}{2}}/r_0 = 0.4$, which corresponds to 87% completion of the diffusint process. Consequently, for small values of $D^{\frac{1}{2}}t^{\frac{1}{2}}/r_0$, it follows that both $D^{\frac{1}{2}}/r_0$ and $(V_e - V_0)$ may be obtained from a plot of $dV_t/dt^{\frac{1}{2}}$ versus $t^{\frac{1}{2}}$ by noting S and I, the slope and intercept respectively, which are related to the required unknowns as follows :

$$D^{\frac{1}{2}}/r_0 = -S/I\pi^{\frac{1}{2}} \quad\text{...(11)}$$

$$V_e - V_0 = I\pi^{\frac{1}{2}}/(6D^{\frac{1}{2}}/r_0) \quad\text{.......................................(12)}$$

The oversimplification involved in equation (2) is clearly demonstrated in Fig. 4 by the fact that $dV_t/dt^{\frac{1}{2}}$ is not constant for small values of time.

As an example of the use of this technique, reference may be made to Fig. 2 in which a plot of $dV_t/dt^{\frac{1}{2}}$ versus $t^{\frac{1}{2}}$ was prepared by numerical differentiation from the corresponding set of cumulative volume observations. From the slope and intercept of this plot, equations (11) and (12) were used to obtain $D^{\frac{1}{2}}/r_0 = 0.0129$ sec.$^{-\frac{1}{2}}$ and $(V_e - V_0) = 1.77$ cm.^{3} These values agree well with the values given in Table II, which were obtained by a digital computer by the computational procedure described for large values of $D^{\frac{1}{2}}t^{\frac{1}{2}}/r_0$.

Results

Some of the results which were obtained for the flow of gases of different molecular dimensions from the Linde Type A synthetic zeolites are given below. Table I has been included to illustrate the reproducibility of the experimental results. It may be seen that, within experimental error, loading pressure $(P_0 - P_a)$ has no effect upon the parameter $D^{\frac{1}{2}}/r_0$; consequently it must be concluded that no error was introduced by assuming the diffusivity to be independent of concentration.

Table II summarises the results obtained for the nitrogen/zeolite 3A system at different temperatures. The experimental observations for the run at $T_t = 303°c$ are shown in Fig. 2.

Although both computational procedures are applicable in the range of moderate values of $D^{\frac{1}{2}}t^{\frac{1}{2}}/r_0$, the digital computer was capable of carrying out the computation in about 10 sec. and was therefore employed to obtain all the results appearing in Tables I and II. The computation procedure for small values of $D^{\frac{1}{2}}t^{\frac{1}{2}}/r_0$ could equally well have been used to obtain many of the results tabulated above.

For each synthetic zeolite system investigated, the corresponding diffusivity was correlated by the conventional relationship

$$D = D_0\exp(-E/RT) \quad\text{.....................................(13)}$$

Since the value of r_0 is frequently subject to uncertainty, the temperature dependencies of $D^{\frac{1}{2}}/r_0$ for the nitrogen/zeolite 3A system were obtained by plotting $\log_{10}(1000\ D^{\frac{1}{2}}/r_0)$ against $(1000/T)$ as shown in Fig. 5. For other systems investigated, the parameters $D_0^{\frac{1}{2}}/r_0$ and E were evaluated in this manner. The results are summarised in Table III.

Discussion

From the smoothness of the results presented graphically in Fig. 2, it is clear that the experimental method was successful in eliminating errors due to fluctuations in room temperature and furnace temperature. Also the excellent agreement which was obtained with the theory, as evidenced by the linearity of the $dV_t/dt^{\frac{1}{2}}$ curve of Fig. 2, indicates the absence of any significant deviation from the theory. In order to avoid any graphical procedure which might have introduced some bias into the final $dV_t/dt^{\frac{1}{2}}$ values, the differentiation was carried out by applying two successive processes of smoothing by groups of three followed by the computation of first differences.
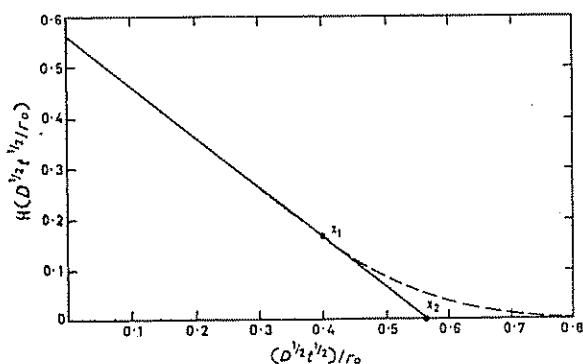
Fig. 4. *Graphical representation of* $H(D^{\frac{1}{2}}t^{\frac{1}{2}}/r_0)$
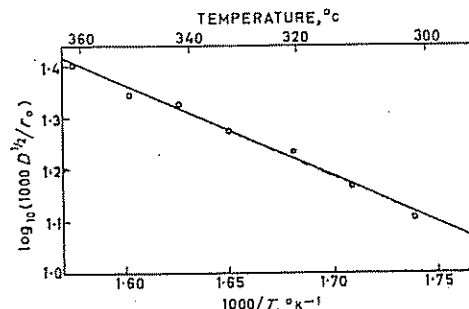*defined by equation* (10)

Fig. 5. *Activation energy plot for nitrogen/
zeolite 3A system*
$E = 16.2$ kcal. mole^{-1}

Table I

Diffusion of propane from the Linde Type 5A synthetic zeolite

T_t, °C	(P_0-P_a), cm. Hg	T_t, °C	P_a, cm. Hg	$D^{\frac{1}{2}}/r_0$, sec.$^{-\frac{1}{2}}$	(V_e-V_0), cm.^{3}
	13.4	28.7	73.5	0.0165	2.01
	17.9	28.3	73.5	0.0166	2.64
28.0	22.6	30.2	73.0	0.0158	3.18
(mean)	28.4	26.1	73.4	0.0163	4.22
	41.2	26.4	73.3	0.0160	5.77
	41.6	28.6	72.6	0.0165	6.03

Table II

Diffusion of nitrogen from the Linde Type 3A synthetic zeolite

T_t, °C	(P_0-P_a), cm. Hg	T_a, °C	P_a, cm. Hg	$D^{\frac{1}{2}}/r_0$, sec.$^{-\frac{1}{2}}$	(V_e-V_0), cm.^{3}
293	28.2	30.9	73.5	0.0116	1.73
303	28.2	30.4	73.6	0.0128	1.76
313	29.9	28.5	73.6	0.0148	1.60
323	29.0	29.9	73.7	0.0172	1.47
334	29.7	29.2	73.6	0.0189	1.42
343	29.9	29.5	73.9	0.0213	1.40
352	30.4	28.1	73.4	0.0222	1.24
363	29.1	29.4	73.5	0.0253	1.13

Table III

*Rate parameters for some common gases diffusing through the
Type A synthetic zeolites*

Gas/zeolite system	Temp. range studied, °C	$D_0^{\frac{1}{2}}/r_0$, sec.$^{-\frac{1}{2}}$	E, kcal.mole^{-1}
Propane/5A	28—360	0.025	0.54
Propane/4A	302—370	0.61	8.7
Ethane/4A	103—254	0.13	3.0
Argon/3A	280—400	6.2	14.0
Nitrogen/3A	293—363	15.8	16.2

If, by selecting a favourable temperature for the diffusion process and/or by using a sample having a favourable value of r_0, the value of $D^{\frac{1}{2}}/r_0$ can be preselected to fall within the range 0.01—0.03, improved diffusivity estimates can be obtained. Most previous investigators appear to have avoided this range by using equation (3) under conditions approaching equilibrium, or by using equation (4) under conditions far removed from equilibrium. Under these conditions, by ignoring small terms in each expansion, equations (3) and (4) provide the following relations

$$\ln\left(\frac{V_t-V_e}{V_0-V_e}\right) = \ln\frac{6}{\pi^2} - \frac{D\pi^2 t}{r_0^2} \quad\quad\dotfill (14)$$

and

$$\frac{V_t-V_0}{V_e-V_0} = \frac{6}{\pi^{\frac{1}{2}}}\left(\frac{Dt}{r_0^2}\right)^{\frac{1}{2}} - \frac{3Dt}{r_0^2} \quad\quad\dotfill (15)$$

Equation (14), which should apply for $D^{\frac{1}{2}}t^{\frac{1}{2}}/r_0$ sufficiently large, is unsatisfactory because the rate of diffusion is very slow within its range of validity and has, therefore, not been employed in the course of this study. On the other hand, although the complete solution in the form of equation (3) was used to obtain the values of $D^{\frac{1}{2}}/r_0$ quoted in the previous section, it has been shown that equation (15) may be used to estimate both $D^{\frac{1}{2}}/r_0$ and $(V_e - V_0)$ to an acceptable degree of accuracy. Most previous investigators have used an over-simplified form of this relationship, however, which results in considerable misinterpretation of experimental data. * In some cases, previously published experimental results have shown the existence of a finite derivative with respect to $t^{\frac{1}{2}}$ at a fractional sorption of unity ;[5] and in other cases, the experimental results have been noticeably non-theoretical by comparison with Fig. 3.

The primary objective of presenting experimental results on the Type A synthetic zeolites has been to illustrate the validity of the experimental method and the computational procedures rather than to provide a basis for discussing the dependency of activation energy upon molecular size. However, it is interesting to compare at least two of the activation energies quoted in Table III—those for the diffusion of nitrogen and argon from the type 3A material. The computations of Kington & Laing[11] have raised some doubt as to the applicability of the critical-dimension criterion of the type employed by Breck and co-workers.[12] It is, therefore, of interest to note that the activation energies obtained for nitrogen and argon diffusion from the zeolite 3A material provide support for the Kington & Laing computations. Whereas Breck and co-workers[12] take the critical dimensions of nitrogen and argon as $3 \cdot 0$ Å and $3 \cdot 84$ Å, respectively, the activation energy for the nitrogen/zeolite 3A system is greater than that for the argon /zeolite 3A system.

Acknowledgment

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Nomenclature

A Specific surface area, $cm.^2g.^{-1}$
C Concentration of diffusing gas at time t, mole $cm.^{-3}$
D Gas/solid diffusivity, $cm.^2sec.^{-1}$
E Activation energy, a constant defined by the expression $D = D_0 \exp(-1000E/RT)$, kcal. $mole.^{-1}$
P_a Atmospheric pressure, cm. Hg
P_0 Initial steady-state gas pressure, cm. Hg
R Gas constant, cal. $mole.^{-1}{}^{\circ}c^{-1}$
r_0 Radius of sphere having the same surface area as a given particle of irregular shape, cm.
T Absolute temperature, $^{\circ}$K
T_a Room temperature, $^{\circ}$c
T_f Furnace temperature, $^{\circ}$c
t Time, sec.
V Specific volume, $cm.^3g.^{-1}$
V_e Calculated volumeter reading corresponding to infinite time, $cm.^3$
V_0 Calculated volumeter reading corresponding to zero time, $cm.^3$
V_t Observed volumeter reading at time t, $cm.^3$

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*If A and V are expressed in terms of an equivalent sphere and the second term of equation (15) is ignored, it should be noted that equations (15) and (2) are identical.