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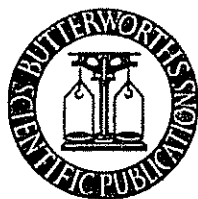
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The Diffusion of Nitrogen and Carbon Dioxide from Coals of Various Rank

S. P. NANDI and P. L. WALKER JR

The diffusion of nitrogen and carbon dioxide from four coals, ranging in rank from low volatile anthracite to high volatile bituminous, was measured over the temperature range from ca. 25° to 140°C. The diffusion is activated, carbon dioxide with each coal having a smaller activation energy than nitrogen. These diffusion results are taken to explain why the surface areas of coals measured by nitrogen adsorption at 77°K are much smaller than those measured by carbon dioxide adsorption at 195°K.

RECENTLY, R. B. ANDERSON and co-workers¹ have concluded that the use of carbon dioxide as an adsorbate at 195°K is an excellent choice if one wishes to obtain closely the total surface area potentially available in coal. P. L. WALKER JR and I. GELLER² previously came to a similar conclusion from studies on anthracite. Both groups of workers find that the carbon dioxide areas are much greater than the areas calculated from nitrogen adsorption at 77°K.

Recent studies by T. G. LAMOND³ give additional insight into these adsorption results on coal. Lamond studied the adsorption of nitrogen (77°K) and carbon dioxide (195°K) on 4A and 5A Linde zeolite molecular sieves. One hour was allowed for each adsorption point. On the 5A sieve, the nitrogen and carbon dioxide areas were 770 and 695 m²/g. On the 4A sieve, the nitrogen and carbon dioxide areas were 1 and 610 m²/g. From these results, by analogy, it appears that coal has a significant number of pores of size close to that of the 4A sieve*.

A number of reasons have been advanced for the major differences in surface areas of coals reported from nitrogen adsorption (77°K) and carbon dioxide adsorption (195°K) including: (1) closure of pores at lower temperatures because of thermal contraction, (2) decreased vibration of the atoms, which surround a pore opening, about their equilibrium position at lower temperatures, and/or (3) activated diffusion. Workers^{4, 5} have ruled out thermal contraction as the major reason for the area differences.

Consider the second possibility suggested. From their studies on zeolites, D. W. BRECK and J. V. SMITH⁶ concluded that molecules having kinetic dimensions close to, but larger than, aperture openings can get into the openings relatively easily because of the thermal vibration of the atoms around the aperture openings. In coal, some of the pores are thought to be lined by parallel platelets of small crystallites. It could be argued that enhanced vibration of the carbon atoms perpendicular to the platelets at 195°K over that at 77°K makes possible a much greater rate of carbon dioxide diffusion into

* There is some question as to the exact size of the aperture openings in 4A zeolite. However, according to Dr D. W. Breck of Linde, a size of 4.0 Å, or slightly less, appears reasonable.

coal. However, recent results by E. A. KELLETT and co-workers⁷, who studied the amplitude of vibration of carbon atoms in two partially graphitized materials appear to rule out this explanation. That is, the amplitude of vibration of the atoms perpendicular to the layer planes of the carbon crystallites increased only 0.022 Å in going from 100° to 300°K. Results on the diffusion of rare gases, ranging from helium to xenon, through 3A Linde zeolite⁸ suggest that such a small change in amplitude of vibration should produce, in itself, only a negligible difference in the activation energy for diffusion of carbon dioxide at 195°K relative to nitrogen at 77°K.

It is, therefore, of interest to investigate whether the carbon dioxide versus nitrogen surface area results can be explained primarily on the basis of activated diffusion of these species into coal. Consequently, the unsteady-state diffusion of carbon dioxide and nitrogen, from coals of different rank, has been studied in this research over a range of temperatures.

EXPERIMENTAL

Coals used

Four coals of 200 × 325 Tyler mesh particle size were used in this study. Analyses of the coals are given in Table 1.

Table 1. Analyses of coals

Coal	State	% Carbon (d.m.f.)	% Volatile (d.m.f.)	% Ash
St Nicholas	Pa	94.0	4.5	9.1
Loree	Pa	93.1	5.4	7.1
Pratt	Ala	86.0	29.2	7.9
Pittsburgh	Pa	82.9	39.5	6.6

Unsteady-state diffusion

This apparatus, experimental procedures, and the computational procedures used to calculate the parameter $D^{1/2}/r_0$ (where D is the diffusion coefficient and r_0 is the diffusion path length) have been described in detail previously⁹. A differential experimental system was used to avoid errors caused by small temperature fluctuations. In principle, the procedure consisted of charging the sample under consideration with nitrogen or carbon dioxide to an absolute pressure of 1204 ± 12 torr (an equilibrium time of about 24 hours was allowed) and then measuring the unsteady-state release of the gas after sudden reduction of the pressure outside the particles back to atmospheric. Before charging the samples with the diffusing gases, they were outgassed for 24 h at temperatures greater than those used in the diffusion measurements.

For computing the diffusion parameter, $D^{1/2}/r_0$, Fick's diffusion equation was assumed to be applicable to the system, with D independent of concentration of the diffusing species. The general solution of Fick's law for a spherical particle, where the external gas pressure is constant, is

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

where V_0 , V_t and V_e are volumes at time $t = 0$, $t = t$ and $t = \infty$. The above equation was used in conjunction with experimental V_t versus $t^{1/2}$ curves to calculate $D^{1/2}/r_0$, V_0 and V_e by a procedure described by E. T. NELSON and P. L. WALKER JR.⁹. ($V_e - V_0$) is the total amount of gas evolved at equilibrium.

The applicability of Fick's law to the gas-solid systems under study was shown by Nelson and Walker⁹. The concentration independence of D has been shown by S. P. NANDI⁸. It was also shown for the nitrogen-coal system that ($V_e - V_0$) varied linearly with charging pressure⁸. Though independent adsorption isotherms are not available, it was concluded that adsorption was linear with pressure from the above observation. Therefore, from ($V_e - V_0$) values obtained for the same charging pressure, at different temperatures, the heat of adsorption could be calculated by application of the van't Hoff equation.

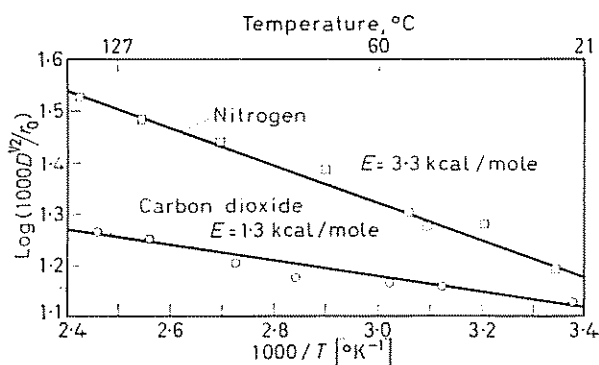


Figure 1. Activation energy plots for the diffusion of nitrogen and carbon dioxide from St Nicholas anthracite

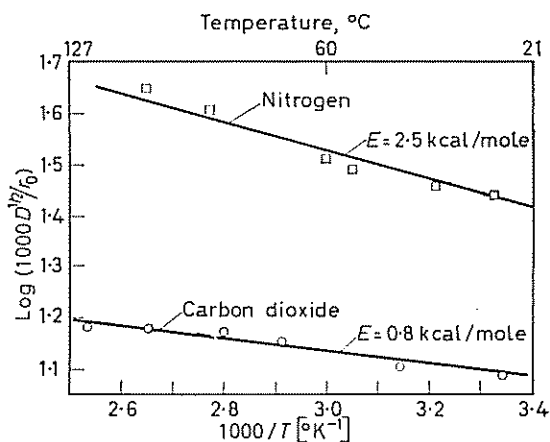


Figure 2. Activation energy plots for the diffusion of nitrogen and carbon dioxide from Loree anthracite

RESULTS AND DISCUSSION

Arrhenius plots for the diffusion of nitrogen and carbon dioxide from the four coals are presented in *Figures 1 to 4*. The diffusion coefficient, D , has not been given since the value of the diffusion path length, r_0 , is unknown at

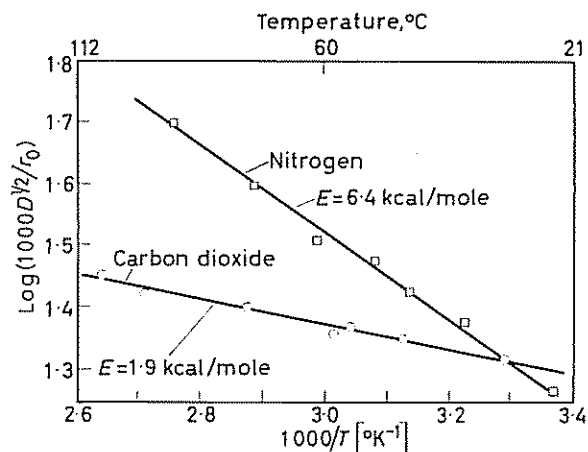


Figure 3. Activation energy plots for the diffusion of nitrogen and carbon dioxide from Pratt coal

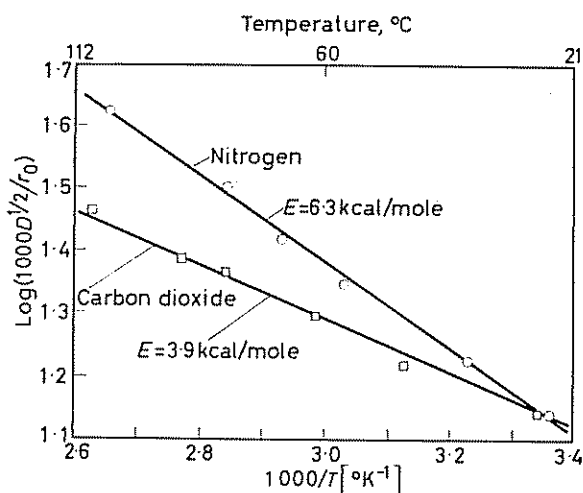


Figure 4. Activation energy plots for the diffusion of nitrogen and carbon dioxide from Pittsburgh coal

present. Studies on the change of $D^{1/2}/r_0$ with particle size clearly show that r_0 is not the particle radius⁸. In any case, we were primarily interested in the activation energy for the diffusion coefficient. Since r_0 should be independent of diffusion temperature and diffusing gas, values of $D^{1/2}/r_0$ will be sufficient for this purpose.

It is seen from *Figures 1 to 4* that the activation energy for the diffusion of carbon dioxide from the coals is always less than the activation energy for the diffusion of nitrogen. On the other hand, the pre-exponential factor is always greater for nitrogen than for carbon dioxide, as is shown in *Table 2*. The result is that the diffusion coefficient of nitrogen into these coals exceeds that of carbon dioxide at temperatures above *ca.* 30°C. However, if these plots can be extrapolated to adsorption temperatures, the diffusion coefficient of carbon dioxide at 195°K will greatly exceed that of nitrogen at 77°K.

Table 2. Pre-exponential factor for the parameter, D^3/r_0 , for the diffusion of nitrogen and carbon dioxide from the coals

Coal	Pre-exponential factor sec^{-1}	
	N ₂	CO ₂
St Nicholas	0.256	0.043
Loree	0.221	0.026
Pratt	4.19	0.098
Pittsburgh	2.79	0.381

Table 3. Volume of gas charged into St Nicholas anthracite prior to diffusion runs

Run temp., °C	$(V_e - V_0)$, cm ³ /g	Free-space volume, cm ³ /g	Volume adsorbed, cm ³ /g
Nitrogen			
26	0.612	0.039	0.573
39	0.493	0.037	0.456
50	0.404	0.036	0.368
54	0.386	0.036	0.350
72	0.295	0.034	0.261
98	0.194	0.031	0.163
120	0.167	0.030	0.137
144	0.133	0.028	0.105
Carbon dioxide			
23	1.368	0.039	1.329
47	1.046	0.036	1.010
58	0.902	0.035	0.867
79	0.646	0.034	0.612
94	0.503	0.031	0.472
118	0.311	0.030	0.281
134	0.226	0.029	0.197

Before considering this extrapolation, it is well to look at the nature of the interaction of nitrogen and carbon dioxide with the coals over the temperature range studied. A consideration of the results on St Nicholas anthracite will suffice to illustrate the situation. *Table 3* summarizes pertinent data on the volume at s.t.p. of gas ($V_e - V_0$) diffusing from the St Nicholas anthracite from the start of a diffusion run to infinite time (that is, when the gas pressure within the particles equals atmospheric pressure). From results on the total pore volume (free-space volume) of St Nicholas anthracite¹⁰, the volume of gas which would diffuse from the sample at particular conditions of charging pressure and temperature, assuming no adsorption and the

perfect gas law, is also given in *Table 3*. It is seen that most of the nitrogen and carbon dioxide charged into St Nicholas anthracite prior to diffusion runs up to the maximum temperature studied is adsorbed. As expected, the fraction of the total gas charged which is adsorbed decreases with increasing temperature. Using the van't Hoff equation, heats of adsorption of 3.2 and 4.3 kcal/mole are calculated for nitrogen and carbon dioxide respectively.

There might be concern about extrapolation of the Arrhenius plots to 195° and 77°K because of increasing adsorption with decreasing temperature and the possibility of enhanced surface diffusion¹¹. For example, E. WICKE and R. KALLENBACH¹² studied the diffusion of carbon dioxide through active charcoal from 0° to 300°C. At temperatures close to 300°C the diffusion coefficient increased slowly with temperature. However, at intermediate temperatures the temperature coefficient of diffusion decreased to zero and, at the lowest temperatures, was negative. They attributed their results to the contribution of surface diffusion where the surface concentration of adsorbed carbon dioxide for a fixed carbon dioxide pressure increased rapidly with decreasing temperature. That is, with charcoal, which has the majority of its micropores in the size range 15 to 20 Å, flow can occur by normal gas phase diffusion plus surface diffusion of an adsorbed layer within the same pores. By contrast, in the present studies the slow diffusion which is being measured is occurring in pores of molecular size, where both gas phase diffusion and surface diffusion are not occurring simultaneously, because of obvious space limitation. The gas molecule always remains in the force field of the solid until it makes its final escape. The process is somewhat analogous to conventional surface diffusion, the only difference being that a number of solid surfaces (at least two) are involved. Therefore, a change in the temperature coefficient of diffusion with temperature would not be expected here. Results for the four coals studied from *ca.* 20° to 140°C support this conclusion.

It is of interest to calculate values of $D^{1/2}/r_0$ at 195° and 77°K. For St Nicholas anthracite, extrapolation of *Figure 1* gives $8.03 \times 10^{-3} \text{ sec}^{-1/2}$ for carbon dioxide at 195°K and $5.40 \times 10^{-6} \text{ sec}^{-1/2}$ for nitrogen at 77°K. To a first approximation, these results can be used in conjunction with the general solution of the unsteady-state diffusion equation¹³ to calculate the fraction of the pore volume of the St Nicholas anthracite filled for particular diffusion times. That is, the general solution gives the fraction of the pore volume ($V_t - V_0$) filled as a function of $D^{1/2}t^{1/2}/r_0$, where t is the diffusion time. Taking a diffusion time of 30 min, it is estimated that 0.80 of the pore volume of St Nicholas anthracite will be filled with carbon dioxide at 195°K. On the other hand, an insignificant fraction of the pore volume will be filled with nitrogen at 77°K. Any reasonable increase in diffusion time for nitrogen at 77°K will produce an insignificant increase in volume filled. For the other coals, the fraction of pore volume filled with carbon dioxide at 195°K ranges from 0.86 for the Loree to 0.32 for the Pittsburgh coal. In all cases, negligible filling of the pore volume with nitrogen will occur.

It is well to emphasize what pore volume was being considered in the above calculations. It was pore volume in pores through which the nitrogen

molecule requires a substantial activation energy to pass (as measured in *Figures 1 to 4*). Therefore, as reasoned previously, the pores would certainly be less than 5 Å in diameter and probably less than *ca.* 4 Å. The surface areas of St Nicholas anthracite, as given¹⁰ by nitrogen adsorption (77°K) and carbon dioxide adsorption (195°K) using an equilibration time of 30 min, were 32.3 and 220 m²/g. The fact that the nitrogen surface area is significant is taken to mean, on the basis of the above calculations, that St Nicholas anthracite has significant area in pores above *ca.* 4 Å. The fact that the area calculated from carbon dioxide adsorption is much higher than the nitrogen area is in line with the above calculations, which indicate that an appreciable fraction of the pores less than *ca.* 4 Å should be filled with carbon dioxide after a diffusion time of 30 min.

It is of interest to consider the values of the activation energies and pre-exponential terms for the diffusion parameters, D^3/r_0 , somewhat further. As discussed by G. L. KINGTON and W. LAING¹⁴, when the size of a diffusing species closely approaches the size of the aperture through which it passes, the activation energy for passage increases sharply with an increase in the kinetic diameter of the diffusing species. Experimentally, the effect of diameter of diffusing species on activation energy was shown to be of major importance by Nandi⁸, who studied the diffusion of five rare gases through 3A Linde zeolite. The activation energy increased monotonically from less than 1 kcal/mole for helium to 19 kcal/mole for xenon. Kinetic diameters of nitrogen and carbon dioxide, as calculated from viscosity data using the Lennard-Jones 6-12 potential energy expression¹⁵, are 3.68 and 3.99 Å respectively. On the basis of these values, nitrogen should have a smaller activation energy for diffusion from the coals than does carbon dioxide. It is significant, however, that these diameters are characteristic of the freely rotating molecules. Since nitrogen and carbon dioxide are non-spherical molecules, they undoubtedly lose some rotational freedom in passing through apertures of molecular size, so that their long axis closely coincides with the centreline of the aperture. T. KIHARA¹⁶ generalized the Lennard-Jones model of spherical molecules to non-spherical molecules, without sacrificing analytical integrability of the second virial coefficient. Assuming nitrogen and carbon dioxide to be spherocylindrical molecules, he obtained the following dimensions: for nitrogen—length, 4.6 Å and width, 3.5 Å; for carbon dioxide—length, 5.8 Å and width, 3.7 Å. Again, on this basis, the activation energy for carbon dioxide diffusion should be greater than that for nitrogen.

To see whether activation energy results on the coals are unusual or whether they appear to be of general occurrence, the diffusion of carbon dioxide⁸ and nitrogen⁹ from 3A Linde zeolite was also studied. Values of D^3/r_0 for carbon dioxide over the temperature range 180° to 600°C could be plotted using the Arrhenius equation to give an activation energy of 4.7 kcal/mole. As previously reported⁹, the activation energy for nitrogen diffusion in 3A zeolite is 16.2 kcal/mole. From the diffusion data on the coals and zeolites (which are chemically dissimilar and possibly also dissimilar in pore structure), it strongly appears that carbon dioxide has a smaller minimum kinetic dimension than does nitrogen—results presented above^{15, 16} to the contrary.

As anticipated, the pre-exponential term for $D^{\frac{1}{2}}/r_0$ was smaller for carbon dioxide than nitrogen for all four coals studied. As mentioned previously, there is expected to be some loss of rotational energy when the molecules pass through the ultrafine pores. This means that the entropy of activation for passage will be negative. Since the rotational partition function of carbon dioxide is greater than that for nitrogen and since it should be necessary for carbon dioxide to lose a greater fraction of its rotational energy to pass through an aperture (because of its greater length), the entropy of activation should be more negative for carbon dioxide. This will result in a smaller pre-exponential term for carbon dioxide.

CONCLUSIONS

For coals of rank varying from low volatile anthracite to high volatile bituminous, diffusion of carbon dioxide and nitrogen from ultrafine pores is found to be activated, with the activation energies for carbon dioxide diffusion less than those for nitrogen. As nitrogen has a kinetic dimension of about 3.7 Å, it is suggested that the minimum dimension of the ultrafine pores may be about 4 Å. Extrapolation of the diffusion parameters, measured between *ca.* 25° and 140°C, to adsorption temperatures shows that a negligible fraction of the ultrafine pores is available to nitrogen at 77°K. On the other hand, a substantial fraction of the ultrafine pores is available to carbon dioxide at 195°K for an equilibration time of only 30 min. Thus, surface areas calculated from carbon dioxide adsorption (195°K) reflect closely the total surface areas of coals, whereas areas calculated from nitrogen adsorption (77°K) indicate the area in pores greater than *ca.* 4 Å. The fact that these surface areas differ considerably for most coals, indicates that coals contain appreciable area in ultrafine pores.

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