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Diffusion of Argon from Coals of Different Rank

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Unsteady state release of argon has been measured from 200x325 mesh samples of 12 coals of volatile matter ranging from 2 to 45% over the temperature range 25°–100°C. The micropore diffusion parameter $(D^{1/2}/r_o)$ has been evaluated. Argon diffusion is found to be activated for all coals except meta-anthracite, which is shown to have lost its microporosity. Activation energies increase monotonically from 3.2 kcal./mole for the anthracite (4.5% VM), to 6.5 kcal./mole for the medium volatile bituminous coal (27.0% VM), and then decrease with further increases in volatile matter to 4.3 kcal./mole for the high volatile bituminous coal (45.4% VM). The magnitude of the activation energies indicates that the size of the micropores in the coals closely approaches the size of the argon atom.

In a recent communication (6) the role of diffusion in establishing equilibrium in the adsorption of nitrogen and carbon dioxide on coals has been clearly indicated. The different internal surface area values obtained from nitrogen adsorption at 77°K. and carbon dioxide adsorption at 195°K. are caused primarily by the different diffusion velocities of the two gases in the micropore structure of coal under the conditions of measurement.

Unsteady state diffusion data obtained by various workers (4, 6, 9, 10, 12) have shown that diffusion of simple gases like methane, nitrogen, oxygen, and argon in coal is activated. That is, diffusion is proportional to $\exp(-E/RT)$ instead of $T^{1.5}$ as in bulk diffusion, or $T^{0.5}$ as in Knudsen diffusion. Diffusion of gases through a porous solid can only become activated if the diameter of the pores (through which diffusion occurs) is comparable with the diameter of the diffusing gas. When the diameter of the gas molecules becomes greater than that of the pores, the activation energy of diffusion increases sharply.

Therefore, data on the activation energy for the diffusion of a noble gas fro coals of different rank permit an estimate of, at least, the trend of micropc size in coal with rank.

The only published work on the diffusion of gas in coals of different rank appears to be that of Bolt and Innes (2) who studied the diffusion of carbon dioxide from eleven samples of coal at 38°C. They found the diffusion coefficient to range from 3.5 to 9.2 x 10^{-8} sq. cm./sec., with no apparent correlation with coal rank. Diffusion data on coals of different rank at temperatures higher than 38°C. have only been reported by the present authors (6). It has been shown (7) that the diffusion of inert or noble gases from coal above room temperatures can be rigorously analyzed by using simple diffusion theory, and that true diffusion parameters of the micropore systems can be obtained. In this paper our measurements on the unsteady state release of argon from coals of various rank, over a temperature range, are reported.

Experimental

Coals Used. Twelve coals of 200 × 325 Tyler mesh particle size were used in this study. Analyses of the coals are given in Table I.

Table I. Analyses of Coals

| Coal | State | Composition, as Received, Wt % | | | | | Volatile Matter |
		H_2O	Ash	C	H	S	% daf
Meta-anthracite	R. I.	0.7	43.5	55.1	0.2	....	2.1
St. Nicholas	Pa.	1.6	9.1	84.2	2.4	0.5	4.5
Dorrance	Pa.	0.7	9.9	82.9	2.5	0.7	5.8
Treverton	Pa.	0.5	9.7	.....	.	1.1	9.0
Upper-Kittanning	Pa.	0.5	9.5	80.4	4.2	1.4	18.0
Kelley	Pa.	0.7	4.7	82.9	5.7	....	27.2
Pratt	Ala.	0.8	7.9	78.8	4.8	1.6	29.2
Upper-Freeport	Pa.	0.4	7.9	79.8	5.0	1.6	33.0
Pittsburgh	Pa.	1.1	5.6	77.5	5.3	1.5	37.4
Pittsburgh	Pa.	1.4	6.6	76.2	5.4	2.2	39.5
Pittsburgh 8	Ohio	1.5	16.4	65.5	4.9	4.5	42.4
Illinois No. 6	Ill.	1.9	7.6	66.1	5.5	2.8	45.4

Unsteady State Diffusion. The apparatus, experimental procedures, and the computational procedures used to calculate the diffusion parameter $D^{1/2}/r_o$ (where D is the diffusion coefficient and r_o is the diffusion path length) have been described in detail previously (6, 8). 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 argon 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 suddenly reducing the pressure outside the particles back to atmospheric.

Prior to being charged with argon, the coal samples were degassed for 24 hours temperatures ranging from 450°C. for the anthracites to 130°C. for the lowest rank Illinois coal. The temperatures of degassing were in every case higher than the temperatures of diffusion measurements. The temperature range over which diffusion was investigated was 25°–100°C.

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

$$\frac{V_t - V_o}{V_r - V_o} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(\frac{-Dn^2\pi^2 t}{r^2_o}\right)$$

where V_o, V_t and V_r are volumes at time $t = 0$, $t = t$, and $t = \infty$. The above equation was used in conjunction with experimental V_t vs. $t^{1/2}$ curves to calculate $D^{1/2}/r_o$ by a procedure described by Nelson and Walker (8).

Results and Discussion

The experimental diffusion parameters, $D^{1/2}/r_o$, at 30°C. are presented in Table II for all the coals. Clearly, no correlation exists between diffusion parameter and rank. If r_o is taken as the average particle radius for the 200 × 325 mesh samples, an upper limit to the values of diffusion coefficient, D, is obtained. The diffusion coefficient ranges from 1.92×10^{-9} sq. cm./sec. for Kelley coal to 1.41×10^{-8} sk. cm./sec. for the Dorrance anthracite. Our previous studies on the change of $D^{1/2}/r_o$ with particle size suggested that r_o is not necessarily the particle radius (7) but is a smaller distance related to the average length of the micropores in the particles. That is, the calculated

Table II. Diffusion of Argon from Coals of Different Rank

Coal	$D^{1/2}/r_o$ at 30°C. sec.$^{-1/2}$	$D_o^{1/2}/r_o$ sec.$^{-1/2}$	Activation Energy kcal./mole
St. Nicholas	0.0182	0.262	3.2
Dorrance	0.0424	0.785	3.6
Treverton	0.0181	0.603	4.2
Upper-Kittanning	0.0261	2.53	5.5
Kelley	0.0157	3.47	6.5
Pratt	0.0229	3.33	6.0
Upper-Freeport	0.0197	1.92	5.5
Pittsburgh	0.0172	0.676	4.3
Pittsburgh	0.0169	2.49	6.0
Pittsburgh 8	0.0193	1.13	4.9
Illinois No. 6	0.0279	1.00	4.3

diffusion coefficients varied with particle size when r_o was taken as the average particle size in a sieve size fraction.

The temperature dependence of the diffusion parameter for all coals could be described by Arrhenius plots. Figure 1 shows typical plots for two of the bituminous coals. Table II summarizes the activation energy and pre-exponential data for all coals, where $D^{1/2}/r_o = D_o^{1/2}/r_o \exp(-E/2RT)$. Since r_o should be independent of diffusion temperature, the activation energy
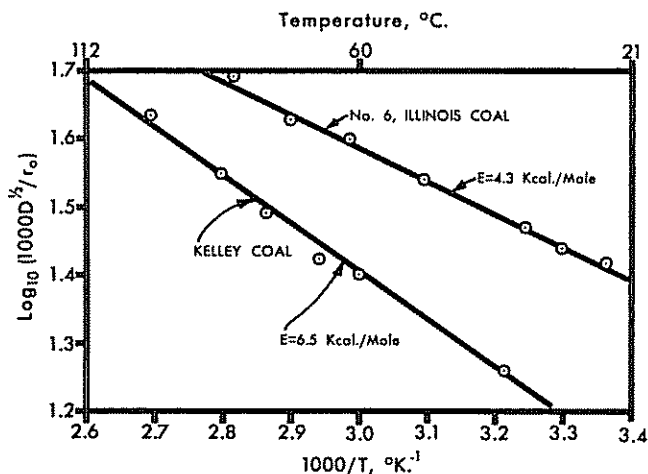

Figure 1. Activation energy plot for the diffusion of argon from two coals (200 × 325)

values can be taken as representing the temperature dependency of the diffusion coefficient. In Figure 2 the activation energy values for argon diffusic are plotted against volatile matter content of the coals. A volcano-shapeu curve is obtained with its peak at a volatile matter content of ca. 27% (carbon content on daf basis of ca. 87%). The correlation towards the high volatile coals shows some spread which is not understood at this time. Two curves are drawn on the high volatile matter side of the curve primarily to emphasize the spread of values.

Curves of helium density (11), heat of wetting (1), and butane adsorption (3) vs. coal rank show minima at ca. 85–90% carbon content. These results are consistent with the correlation between activation energy for diffusion and coal rank found in this paper. A maximum in activation energy between 85 and 90% carbon indicates that the average size of the micropores in coal goes through a minimum at this point. This would result in the internal microporosity in coals of 85–90% carbon content being most inaccessible to displacement and adsorbing fluids.

The meta-anthracite sample behaved in a completely different way compared with the rest of the coals. It had a negligible capacity for argon; consequently, diffusion measurements could not be made. Helium, even at 250°C., could not enter into its micropores. Helium was shown to be able to pene-
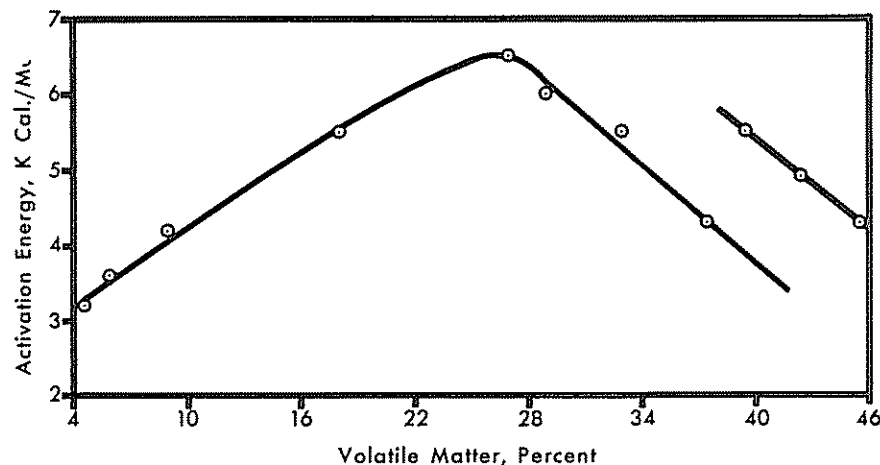
*Figure 2.   Activation energy for the diffusion of argon from coals (200 × 325)
of different rank*

trate the pores of a 1700°C. heat-treated St. Nicholas anthracite at 200°C. (7) even though heat treatment at this temperature removed most of its microporosity. From this, it appears that the meta-anthracite has a very small microporosity.

This result is to be expected from the x-ray structure of meta-anthracites. Ergun *et al.* (5) showed that a significant degree of graphitization in anthracite by the natural process of metamorphism is attained when the graphite-like layers reach a size of 25–30A. In the same paper it was shown that the r_c and L_a values for a meta-anthracite were 200 and 2500A., respectively, compared with values of 20 and 30A for the L_c and L_a dimension of a typical anthracite. The x-ray diffraction pattern of the meta-anthracite was strikingly similar to the pattern given for Ceylon graphite. From these evidences, meta-anthracite should be considered to be a highly graphitic substance and consequently nonporous.

Conclusions

The results of argon diffusion from coals have shown that the minimum size of the micropore system in coals is a function of the rank. The activation energy values show that the critical dimension of the pores go through a minimum in the range of good coking coals. Because the diffusion of argon is activated, it is concluded that the minimum dimension of the micropores is comparable to the size of the argon atom.

The critical dimension of the micropores in anthracite is large compared with that in coking bituminous coal, but when the meta-anthracite region is reached the microporosity disappears.

The minimum dimension of the micropores increases in the low rank coals, but the correlation between rank and activation energy is poor in this

region. Bituminous coals are more complex than anthracites. They cont.-'
varying proportions of the petrological components, with these compone.,
undoubtedly having different micropore properties. Therefore, with bitumi-
nous coals, petrologically homogeneous components should be studied.

Acknowledgments

Literature Cited

(1) Berkowitz, N., *Can. J. Technol.* **33**, 169 (1955).
(2) Bolt, B. A., Innes, J. A., *Fuel* **38**, 333 (1959).
(3) Gregg, S. J., Pope, M. I., *Fuel* **38**, 501 (1959).
(4) Joy, A. S., *Conf. Sci. Use Coal, Sheffield, 1958,* **A–67** (1958).
(5) Mentser, M., Donnell, H. J., Ergun, S., *Fuel* **41**, 153 (1962).
(6) Nandi, S. P., Walker, P. L. Jr., *Fuel* **43**, 385 (1964).
(7) Nandi, S. P., Ph.D. Thesis, Pennsylvania State University, 1964.
(8) Nelson, E. T., Walker, P. L., Jr., *J. Appl. Chem.* **11**, 358 (1961).
(9) Pruss, W., 2nd Intern. Conf. Coal Sci., *Brennstoff-Chemie* **S35** (1958).
(10) Sevenster, P. G., *Fuel* **38**, 403 (1959).
(11) Van Krevelen, D. W., Schuyer, J., "Coal Science," p. 153, Elsevier Publishing
   Co., Amsterdam, 1957.
(12) Zwietering, P., Overeem, J. F., Van Krevelen, D. W., *Fuel* **35**, 66 (1956).

Discussion

George Kapo. What is the cause of the minimum in pore diameter y
observed as one increases the percent carbon in the coal?

S. P. Nandi. Many parameters (e.g., helium density, heat of wetting,
butane adsorption, etc.) for correlating coal rank pass through a minimum at
ca. 85–90% carbon content. In the present paper another parameter—the
average size of the micropores—has been shown to follow the same pattern.

One plausible explanation of the above phenomenon can be given as fol-
lows. During the biochemical change from wood to peat, with the production
of a hydrosol, there is a pronounced swelling, and the greater proportion of
the water is contained in the bigger capillaries. The loss of moisture during
the production of the hydrogel of lignite is accompanied by shrinkage of the
larger pores without much diminution in the number or size of the smaller
pores. The change from lignite to bituminous coal is a continuation of the
process of conversion of peat to lignite, with a continued loss of water and a
reduction in the number of pores of all sizes, but especially of the larger pores,
until a carbon content of about 89% is reached. With further increase in rank
the liberation of methane (as a result of carbon to carbon bond formation)
again increases the porosity of coal (W. Francis, "Coal," pp. 667–716, Edward
Arnold Ltd., London, 1961).

Bhupendra K. Mazumdar. Dr. Nandi mentioned that prior to diffusion studies, degassing the anthracite sample was carried out at 450°C. or so, and he commented that such high temperatures could be used satisfactorily. However, we wonder if this temperature of treatment is safe since, in our experience, at this temperature pyrolysis may set in to a certain extent.

Dr. Nandi. Outgassing at 450°C. is thought to have produced a negligible change in the ultrafine structure of St. Nicholas and Dorrance anthracites (S. P. Nandi, V. Ramadass and P. L. Walker, Jr., *Carbon* 2, 199 (1964)). The carbon dioxide surface areas of raw and 700°C. heat-treated St. Nicholas anthracite are 220 and 215 sq. meters/gram, respectively, and those for the raw and 500°C. heat-treated Dorrance are 215 and 235 sq. meters/gram, respectively. In case of the higher volatile matter Treverton anthracite, this outgassing temperature apparently produced a significant change.