

# CHANGES IN THE ULTRAFINE STRUCTURE OF ANTHRACITES UPON HEAT TREATMENT

S. P. NANDI, V. RAMADASS and P. L. WALKER, Jr.

Department of Fuel Technology, Pennsylvania State University, University Park, Pennsylvania

(Received 6 April 1964)

**Abstract**—Changes in the ultrafine structure of three 200 × 325 mesh Pennsylvania anthracites, of VM ranging from 4.5 to 9.0 per cent, upon heat treatment in an oxygen-free atmosphere have been followed. After going through slight maxima at lower HTT, the total surface areas decreased sharply upon heat treatment at 900°C. Helium and mercury densities increased monotonically with increasing HTT. Unsteady-state diffusion of gases from the anthracites has been measured. The diffusion rate decreased sharply and continuously upon heat treatment at temperatures between 600 and 1700°C, primarily because of a steady increase in activation energy for diffusion. The increase in activation energy is attributed to a continuous decrease in the size of the ultrafine pores with increasing HTT.

## 1. INTRODUCTION

It is well known that the ultrafine structure of anthracite exhibits molecular-sieve properties.<sup>(1-6)</sup> It has further been shown that upon using appropriate activation procedures (during the reaction of anthracite with carbon dioxide at elevated temperatures) a large increase in adsorption capacity and rate of adsorption can be obtained in the ultrafine structure while still retaining its molecular-sieve behavior.<sup>(6)</sup> Little quantitative data are available, however, on the changes produced in the ultrafine structure of anthracite upon thermal treatment to elevated temperatures in the absence of oxidizing gases. Such information is important when calcined anthracite is to be used as a filler in electrodes, anodes, cell liners and plastics. In this paper, the change in the ultrafine structure of three anthracites upon heat treatment has been followed using conventional techniques (gas adsorption and density measurements) and the newer technique (unsteady-state diffusion of gases from the ultrafine structure).

## 2. EXPERIMENTAL

### *Anthracites used*

Three Pennsylvania anthracites of 200 × 325 Tyler mesh were used in this study. The analyses of the anthracites used are given in Table 1.

TABLE 1. ANALYSES OF ANTHRACITES

Coal	% Carbon (d.m.f.)	% Volatile (d.m.f.)	% Ash
St. Nicholas	94.0	4.5	9.1
Dorrance	92.7	5.8	9.9
Treverton	92.0	9.0	9.7

### *Heat treatment*

Heat treatment up to 1000°C was carried out in a tubular furnace, with the power input to the furnace controlled by a Leeds-Northrup duration-adjusting type program controller. A desired linear heating rate of  $5.0 \pm 0.1^\circ\text{C}/\text{min}$ . and maximum temperatures during soaking within  $2^\circ\text{C}$  could be maintained. Nitrogen of 99.96 per cent purity was passed over the sample (*ca.* 25 g held in a quartz boat) throughout the heating and cooling cycle, after it was first circulated over copper turnings at 550°C to remove traces of oxygen.

In selected cases, heat treatments at temperatures in the range 1200–1700°C were performed in an induction furnace under an atmosphere of helium of 99.98 per cent purity. Desired heating rates and maximum temperatures were obtained by manually adjusting the power input.

### Apparatus to measure properties of anthracites

**Gas adsorption.** The low temperature gas adsorption apparatus used was of the volumetric type, similar to that described by EMMETT<sup>(7)</sup> and shown schematically by KOTLENSKY.<sup>(8)</sup> Prior to measuring free space with helium, the samples were degassed under vacuum at 200°C for 24 hr. Isotherms were obtained for nitrogen at 77°K and carbon dioxide at 195°K. An equilibration time of 30 min was allowed for each measurement. Specific surface areas, calculated from the adsorption data using the BET equation, could be duplicated within  $\pm 2.5$  per cent.

**Mercury density.** Mercury densities were determined by mercury displacement using a mercury porosimeter.<sup>(9)</sup> Prior to measurement, the samples were outgassed in the porosimeter at room temperature for one hour. The volume of mercury forced between the particles was followed by the potential drop across a platinum-iridium wire looped and held taut inside a precision bore section of a dilatometer tube. Complete filling of the void volume between particles was taken as the point where a negligible change in potential drop occurred with an increase in pressure. Densities could be duplicated within  $\pm 0.02$  g/cm<sup>3</sup>.

**Helium density.** Helium densities were determined by the conventional method in which a measured quantity of helium was expanded into a sample holder (held at  $30 \pm 0.1^\circ\text{C}$ ) of known volume containing a sample of known weight. Prior to the measurement, the samples were outgassed at 200°C for 24 hr. A one-hour period was found adequate to reach equilibrium in most cases. Densities could be duplicated within  $\pm 0.03$  g/cm<sup>3</sup>.

**Crystallite height measurements.** X-ray diffraction tracings over the angular range 10–40° ( $2\theta$ ) were made with a General Electric XRD-3 X-ray spectrometer using nickel filtered copper radiation. Crystallite heights were calculated from the (002) band by the Scherrer equation,<sup>(10)</sup> using the "crude" method as recently justified.<sup>(11)</sup> Crystallite heights could be duplicated within  $\pm 0.5$  Å.

**Unsteady-state diffusion.** This apparatus, the 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 previously.<sup>(12)</sup> Briefly, a differential experimental

system was used to avoid errors caused by small temperature fluctuations. In principle, the procedure consisted of charging the particle sample under investigation with the selected gas up to some pressure in excess of atmospheric (by exposure to the gas at the diffusion temperature for 24 hr) and then measuring the unsteady-state release of the gas after sudden reduction of the pressure outside the particles back to atmospheric. The charging pressure never exceeded 2 atm and usually was *ca.* 1.7 atm. Prior to charging the samples with gas, they were outgassed at 450°C for 24 hr.\* It was essential that the outgassing temperature be higher than the maximum temperature of diffusion measurement, since removal of water and/or occluded gases during the measurement would invalidate the experiment.

**Volatile matter release.** Detailed studies have been made on the kinetics of VM release from anthracites.<sup>(13, 14)</sup> The volume and analysis of the VM release, as a function of temperature, have been measured. Where appropriate, these results will be presented in this paper. The experimental apparatus and procedure have been fully described.<sup>(13)</sup>

TABLE 2. WEIGHT LOSSES UPON HEAT TREATMENT OF THE ANTHRACITES

Anthracite	Heat treatment temperature, °C	Loss in weight %
St. Nicholas	500	1.7
	700	3.7
	800	4.0
	900	3.6
	1000	4.5
Dorrance	500	0.79
	600	4.2
	700	5.2
	800	6.8
	900	4.6
Treverton	500	4.8
	600	6.6
	700	8.4
	800	9.5
	900	10.2

\*Outgassing at 450°C is thought to have produced a negligible change in the ultrafine structure of the St. Nicholas and Dorrance anthracites, as will be seen later from the surface area results. In the case of the higher volatile matter Treverton anthracite, this outgassing temperature apparently produced a significant change in the raw coal.

### 3. RESULTS AND DISCUSSION

#### *Volatile matter release from anthracites*

Prior to examining the change in ultrafine structure of the anthracites upon heat treatment, results on the liberation of VM and the accompanying weight loss during heat treatment should be examined. Samples were heated to maximum temperature at 5°C/min and soaked for 2 hr. Table 2 summarizes the results. Three separate heating runs were made on St. Nicholas and Dorrance anthracites to 800 and 900°C. Weight losses agreed to within  $\pm 2$  per cent.

For the St. Nicholas and Dorrance anthracites, relatively small decreases in weight occurred upon heating to 500°C. In fact, the VM release remained small up to 650°C for the St. Nicholas anthracite, as seen in Fig. 1. Figure 2 shows that a sharp increase in VM release from the St. Nicholas anthracite coincided with the occurrence of substantial amounts of hydrogen and methane in the recovered gas. At heat treatment temperatures (HTT) up to 650°C, the VM primarily consisted of carbon dioxide and carbon monoxide. For the Treverton anthracite, a substantial weight loss

occurred upon heating to 500°C. This is believed to be a result of release of much greater quantities of the oxides of carbon from this anthracite relative to St. Nicholas and Dorrance.

It is of interest that the weight losses for St. Nicholas and Dorrance anthracites were higher for maximum HTT of 700 and 800°C than for a HTT of 900°C, for the particular heating cycle selected. This is thought to be a result of the sharp increase in the H<sub>2</sub>-CH<sub>4</sub> ratio in the product gas with increasing temperatures above *ca.* 750°C, as seen in Fig. 2. The equilibrium H<sub>2</sub>-CH<sub>4</sub> ratio for the reaction,  $C + 2H_2 \rightleftharpoons CH_4$ , is *ca.* 10 at 1000°K and 1 atm total pressure.<sup>(15)</sup> It is seen from Fig. 2 that the H<sub>2</sub>-CH<sub>4</sub> ratio in the VM at this liberation temperature is *ca.* 0.3. This indicates either that a sizeable amount of methane is being produced as a primary product by desorption of functional groups on the coal and then slowly decomposing to produce hydrogen or that the gas pressure within the ultrafine structure of the anthracite is very high. For example, at 1000°K and a total pressure of 100 atm, the H<sub>2</sub>-CH<sub>4</sub> equilibrium ratio is *ca.* 0.3. Heat treatment runs were made on

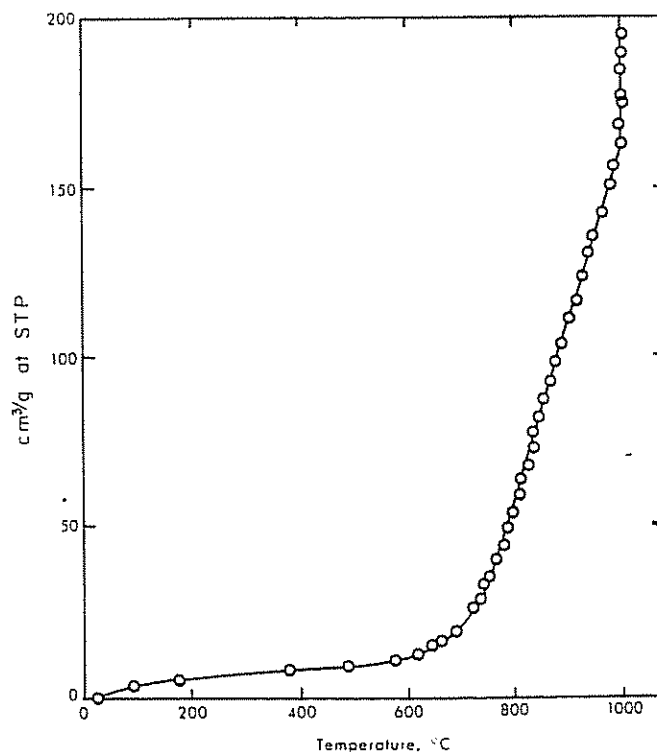


FIG. 1. Relationship between the volume of volatile matter evolved and temperature for St. Nicholas anthracite.

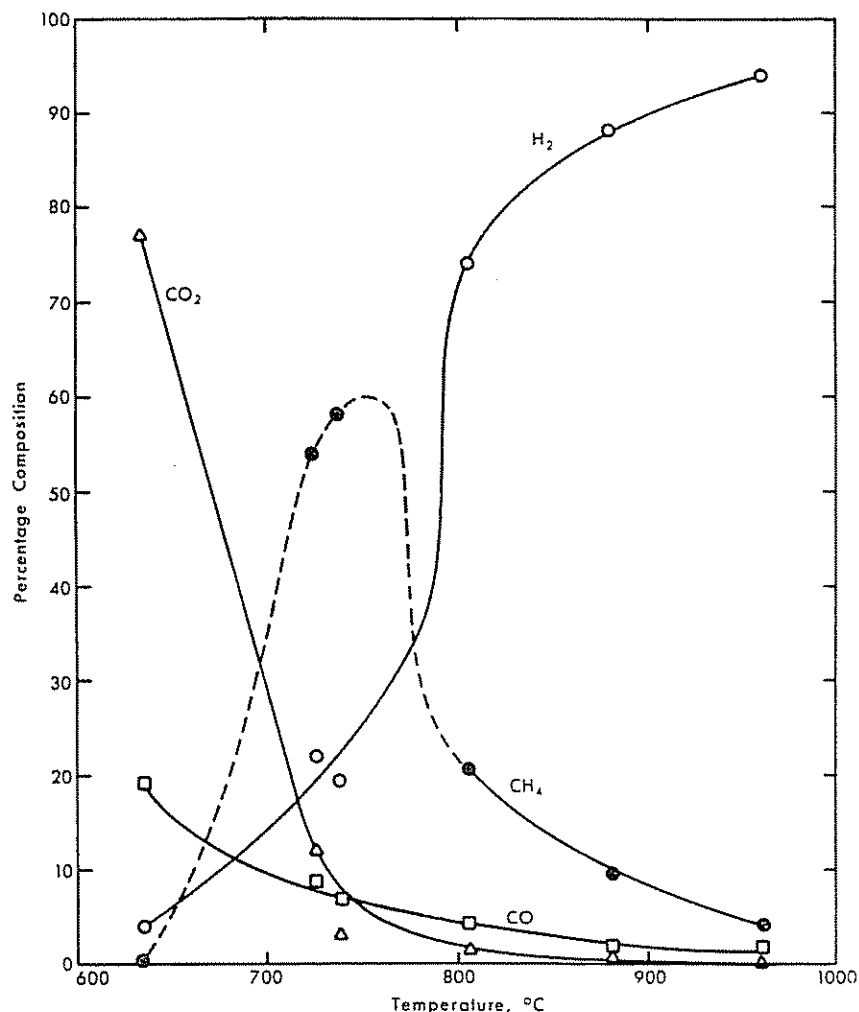


FIG. 2. Relationship between volatile matter composition and temperature for St. Nicholas anthracite.

St. Nicholas anthracite up to 800 and 900°C, but with no soak-time at maximum temperature. In this case, the weight losses were 2.7 and 3.1 per cent respectively. With increasing soak time (and at a value of less than 2 hr), the weight loss for the 900°C HTT eventually falls below that for the 800°C HTT, since the difference in average molecular weight of the total VM produced for these HTT will more than compensate for the larger volume of VM released in the 900°C heat treatment run.

It is noteworthy that the weight loss for the Treverton anthracite did not go through a maximum with increasing HTT. This could be a result of the oxides of carbon making a greater contribution to the total VM for this anthracite and thus

reducing the effect of an increase in the H<sub>2</sub>-CH<sub>4</sub> ratio on the average molecular weight of the VM. Confirming results are not available on this point.

#### Surface areas

Table 3 summarizes the surface area results obtained from nitrogen and carbon dioxide adsorption. As suggested by WALKER and GELLER<sup>(2)</sup> and later supported by ANDERSON, HOFER and BAYER,<sup>(16)</sup> areas calculated from carbon dioxide adsorption at 195°K represent closely the total surface area of coal. On the other hand, nitrogen at 77°K diffuses slowly into pores less than *ca.* 4.5 Å in diameter and thus is not adsorbed by most of the ultrafine structure in coals. For heat treatment temperatures up to 800°C, the anthracites retained their large surface areas. In fact, for the

TABLE 3. EFFECT OF HEAT TREATMENT ON THE SURFACE AREAS OF THE ANTHRACITES

Anthracite	Heat treatment temperature, °C	Surface areas, m <sup>2</sup> /g	
		N <sub>2</sub>	CO <sub>2</sub>
St. Nicholas	raw	32.3	220
	700	24.9	215
	800	9.6	198
	900	5.1	104
	1000	3.7	23.6
Dorrance	raw	34.2	215
	500	38.8	235
	600	23.4	250
	700	10.2	273
	800	6.8	187
	900	1.0	25.9
Treverton	raw	1.5	131
	500	2.8	222
	600	7.2	243
	700	11.5	216
	800	2.3	208
	900	0.8	61.1

TABLE 4. EFFECT OF HEAT TREATMENT ON THE HELIUM AND MERCURY DENSITIES OF THE ANTHRACITES

Anthracite	Heat treatment temperature, °C	Density, g/cm <sup>3</sup>	
		Helium	Mercury
St. Nicholas	raw	1.66	1.47
	700	1.73	1.49
	800	1.80	1.50
	900	1.86	1.56
	1000	2.08	1.61
Dorrance	raw	1.63	1.27
	500	1.64	1.35
	600	1.65	1.42
	700	1.79	—
	800	1.85	1.57
	900	2.06	1.65
Treverton	raw	1.58	1.21
	500	1.63	1.27
	600	1.67	1.36
	700	1.75	1.43
	800	2.05	1.54
	900	2.08	1.65

Dorrance and Treverton samples (and probably St. Nicholas) the surface areas went through a maximum with increasing HTT. The increase in surface area upon heat treatment at the lower temperatures can be attributed to the release of gaseous oxides of carbon, resulting in the opening up of pores which were closed to carbon dioxide adsorption in the raw anthracites. As expected, the Treverton anthracite, which showed the greatest VM release at lower temperatures, also showed the greatest increase in surface area. At HTT above 800°C, the total surface area of the anthracites decreased sharply as the ultrafine pores decreased in size and ultimately became inaccessible to carbon dioxide. This model will be further clarified by the unsteady-state diffusion results. A sizeable activation energy can be attributed to the process which decreased the size of the ultrafine pores. That is, for the 900°C heat treatment run on St. Nicholas anthracite, with no soak time, the area was still 206 m<sup>2</sup>/g.

It is seen, from the nitrogen adsorption results, that the amount of area in pores greater than *ca.* 4.5 Å varied widely. These areas also went through a maximum with increasing HTT. For a HTT of 900°C the areas were particularly low for the Dorrance and Treverton anthracites.

#### Densities and pore volumes

Table 4 presents the helium and mercury density values on a m.m.f.b. The helium and mercury density of the mineral matter in all samples was taken as 2.7 g/cm<sup>3</sup>.<sup>(17)</sup> The helium densities increased with increasing HTT. At low HTT, the helium density would be expected to increase because the release of the gaseous oxides of carbon would open up closed pores. In the intermediate temperature range up to *ca.* 800°C, the release of methane would remove carbon atoms and unblock pores. Further, the release of the low density species, hydrogen, would increase the helium density. At HTT above 800°C, it is suggested that most of the increase in helium density is attributed to a decrease in average size of the closed pores and their ultimate elimination.

As expected from the helium density results, the mercury densities also increased with increasing HTT as seen in Table 4. From the helium and mercury densities, the total open pore volume and porosity of the samples can be calculated. The results are summarized in Table 5. In spite of the large increases in densities with increasing HTT, the total open pore volumes and porosities showed erratic and relatively little change. This indicates that most of the pore volume which was eliminated

TABLE 5. EFFECT OF HEAT TREATMENT ON THE SPECIFIC OPEN PORE VOLUME AND PERCENTAGE POROSITY OF THE ANTHRACITES

Anthracite	Heat treatment temperature, °C	$V_L$ , cm <sup>3</sup> /g	Porosity, %
St. Nicholas	raw	0.07	10.6
	700	0.10	14.2
	800	0.11	16.5
	900	0.10	16.1
	1000	0.14	22.6
Dorrance	raw	0.17	22.1
	500	0.13	17.7
	600	0.10	13.9
	800	0.10	15.2
	900	0.11	18.7
Treverton	raw	0.19	23.2
	500	0.09	11.2
	600	0.14	18.6
	700	0.13	18.3
	800	0.16	25.0
	900	0.13	20.6

upon heat treatment was located in pores already closed to helium.

#### *Crystallite heights*

As shown by transmission electron microscopy studies, pore volume in carbons can be produced by the irregular packing of crystallites.<sup>(17)</sup> Therefore, it is of interest to compare changes in crystallographic parameters upon heat treatment with changes in ultrafine pore structure. Unfortunately, the obtaining of quantitative data on crystallite diameter and interlayer spacing is laborious<sup>(11)</sup> and probably, in any case, not meaningful for samples relatively high in mineral matter. Quantitative crystallite height values can be obtained relatively simply<sup>(11)</sup> (even on impure samples); they are presented in Table 6. No apparent relation exists between the change in crystallite height upon heat treatment and changes in the ultrafine pore structure. As found previously for other raw carbonaceous solids,<sup>(18)</sup> the crystallite height of the raw anthracites decreased upon heat treatment at temperatures between 500 and 900°C. Possible reasons for this have been discussed.<sup>(19)</sup>

It has previously been shown that the closed pore volume in calcined petroleum cokes decreases

sharply with increase in crystallite alignment.<sup>(20)</sup> The relative degree of crystallite alignment can be measured for carbons of essentially the same crystallite size from the relative intensity of their (002) X-ray diffraction peak,<sup>(20, 21)</sup>  $I(002)$  values for the anthracites are presented in Table 6, normalized to 100 for the raw St. Nicholas sample. Relatively minor changes in  $I(002)$  occurred with increasing heat treatment temperature for the anthracites, showing that significant improvement in crystallite alignment did not occur. Therefore, the substantial increase in helium density upon heat treatment to 900°C (part of which is caused by a decreasing closed pore volume) cannot be attributed to enhanced crystallite alignment.

#### *Diffusion parameters*

As considered theoretically by KINGTON and LAING<sup>(22)</sup> for the diffusion of gases through molecular sieve zeolites, when the size of the diffusing species closely approaches the size of the aperture through which it passes, the diffusion becomes activated. Under these conditions a further small decrease in aperture size produces a large increase in activation energy for diffusion. Nelson and Walker showed the validity of this concept experimentally for the diffusion of propane through 4 and

TABLE 6. X-RAY DIFFRACTION RESULTS ON THE HEAT TREATED ANTHRACITES

Anthracite	Heat treatment temperature, °C	Crystallite Height, Å	$I(002)$
St. Nicholas	raw	15.6	100
	700	10.8	105
	800	10.8	97
	900	11.1	103
	1000	13.0	106
Dorrance	raw	18.0	131
	500	15.8	122
	600	13.2	117
	700	11.3	100
	800	15.2	131
Treverton	raw	18.4	100
	500	14.9	96
	600	11.2	80
	700	11.2	78
	800	11.2	86
	900	10.6	94

5 A Linde zeolites, obtaining activation energies of 8.7 and 0.5 kcal/mole respectively.<sup>(12)</sup> The kinetic dimension\* of propane, calculated using the Lennard-Jones potential and viscosity data is 5.1 Å.<sup>(23)</sup>

As indicated previously the parameter,  $D^{1/2}/r_0$ , has been calculated from the diffusion results. The diffusion coefficient,  $D$ , has not been given since the value of the diffusion path length,  $r_0$ , is unknown at present. Studies on the change of  $D^{1/2}/r_0$  with anthracite particle size clearly shows that  $r_0$  is not the particle radius.<sup>(24)</sup> In any case, we were primarily interested in the activation energy for the diffusion coefficient. Since  $r_0$  should be independent of diffusion temperature, values for  $D^{1/2}/r_0$  will be sufficient for this purpose.

A thorough study was made of the diffusion of gases from St. Nicholas anthracite heat treated up to 1700°C. For samples heated to 900°C, the diffusion of nitrogen, ethane and argon was

\*The kinetic dimension is the distance of approach where the potential energy of interaction equals zero.

studied. For samples heated to higher temperatures, it was necessary to use smaller diffusing species in order to have a rate of diffusion which was sufficiently rapid to be measurable in a convenient period of time. Hydrogen and helium were used.

Figure 3 presents Arrhenius plots for the diffusion of nitrogen and ethane out of St. Nicholas anthracite samples heated to a maximum temperature of 900°C. The plots of nitrogen and ethane diffusing from the raw anthracite are not shown, since they fall very close to the 700°C sample. Large decreases in the diffusion parameters of both nitrogen and ethane resulted, however, when the HTT was increased from 700 to 900°C. There also was a significant increase in the activation energy for diffusion of both gases in going from a HTT of 700 to 900°C, indicating a decrease in the average size of the ultrafine pore structure which is determining the diffusion rate. As expected ethane had a higher activation energy for diffusion from comparable St. Nicholas samples than did

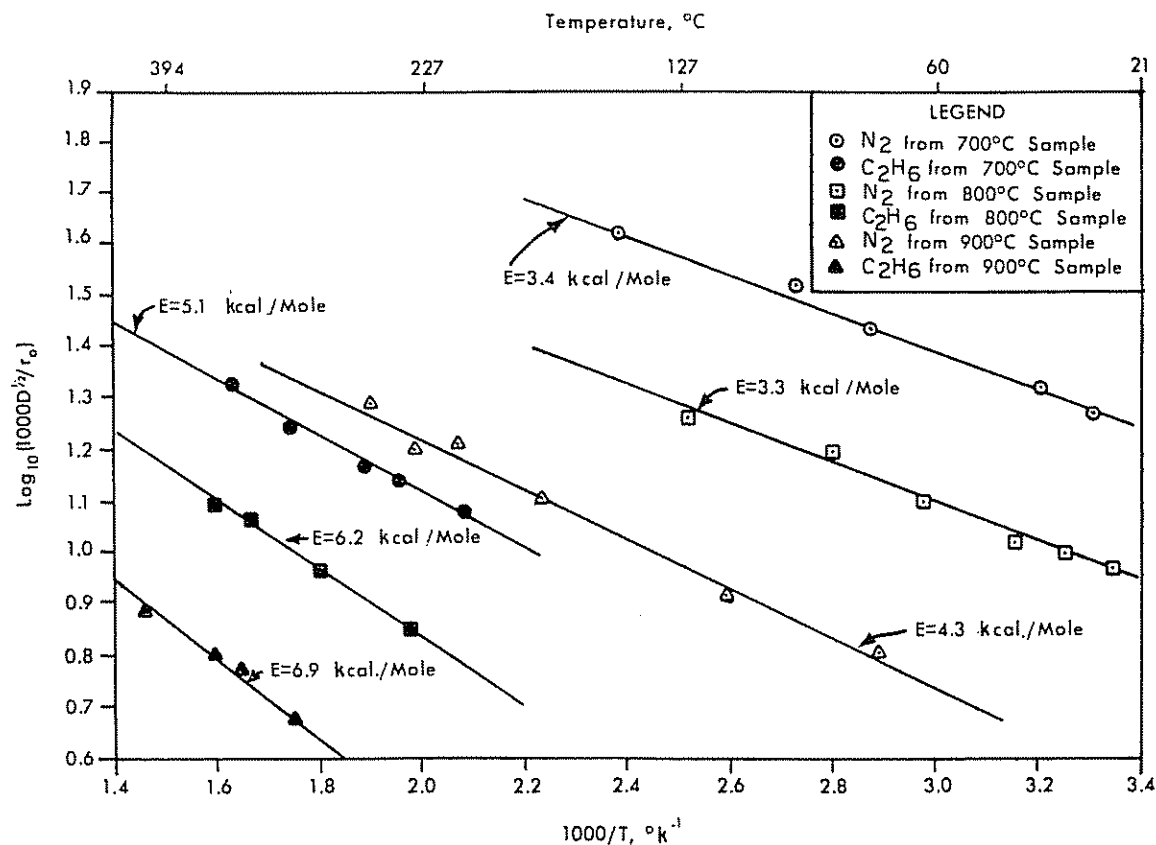


FIG. 3. Activation energy plots for the diffusion of nitrogen and ethane from heat treated St. Nicholas anthracite.



nitrogen. That is, the kinetic dimensions of ethane and nitrogen are 4.41 and 3.68 Å respectively.<sup>(23)</sup> It is noted that there was some increase in the difference in activation energy for ethane and nitrogen diffusion when the St. Nicholas sample was heated to higher temperatures. That is, the difference in activation energy was *ca.* 1.2 /kcal mole for the raw anthracite and *ca.* 2.7 kcal/mole for samples heat treated to 800 and 900°C. This indicates the possibility of producing sharper molecular sieve effects for different gases by heat treating anthracites.

Figure 4 presents Arrhenius plots for the diffusion of helium and hydrogen out of St. Nicholas samples heated at temperatures between 1200 and 1700°C. Considerable experimental difficulties were encountered in these diffusion rate measurements. The ultrafine pore volume of these samples was low; and, hence the volume of gas released was low (*ca.* 0.4 cm<sup>3</sup> at STP for 25 g samples). A slight variation in room temperature affected the rate measurements. Even though the

precision of these measurements was less than that obtained for samples heated to temperatures below 900°C, the Arrhenius plots are reasonably good. There was an increase in the activation energy for the diffusion of helium with increasing HTT. The sample heated to 1400°C had the same activation energy for helium diffusion as the sample heated to 900°C had for nitrogen diffusion. This is strong evidence for a continued decrease in the size of the ultrafine pores with increasing HTT in this temperature range. As expected, hydrogen had a higher activation energy for diffusion out of the 1400°C heat treated sample than did helium. That is, the kinetic dimensions of hydrogen and helium are 2.97 and 2.58 Å respectively.<sup>(23)</sup> It is of interest that the activation energy for helium diffusion from the 3 A Linde zeolite is less than 1 kcal/mole.<sup>(24)</sup> This suggests that the ultrafine pores in the St. Nicholas samples heated to 1400 and 1700°C had a size less than that of the 3 A zeolite.

Figures 5-7 present Arrhenius plots for the diffusion of argon from St. Nicholas, Dorrance and

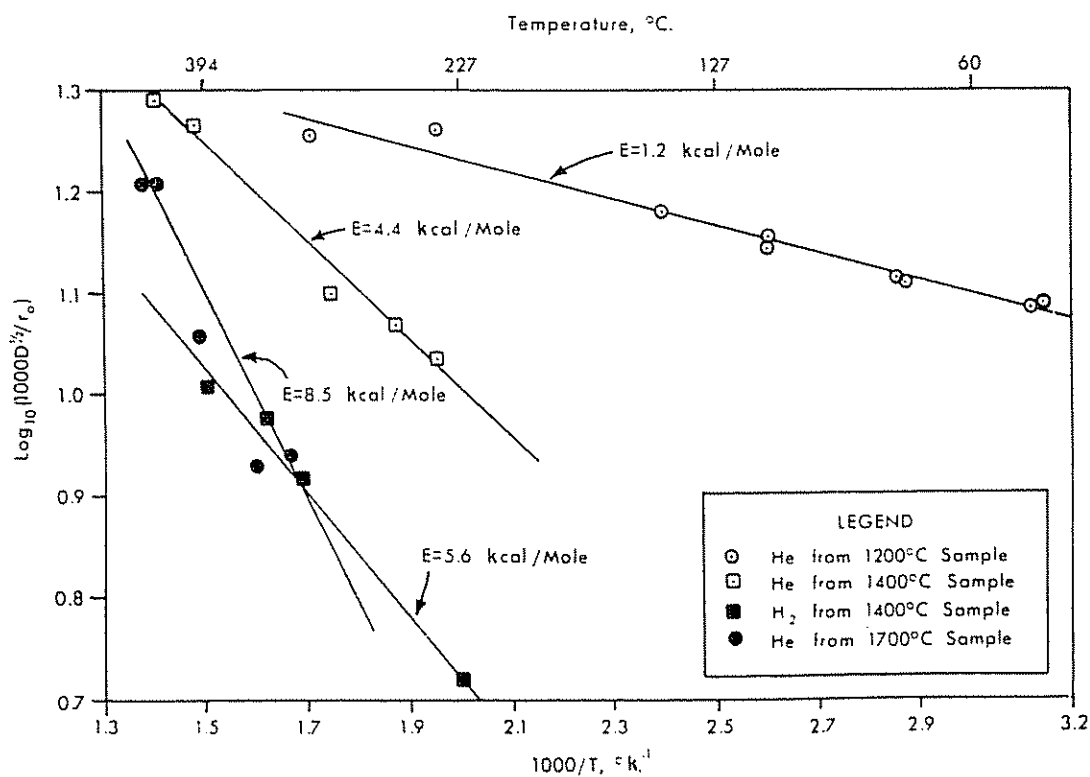


FIG. 4. Activation energy plots for the diffusion of helium and hydrogen from heat treated St. Nicholas anthracite

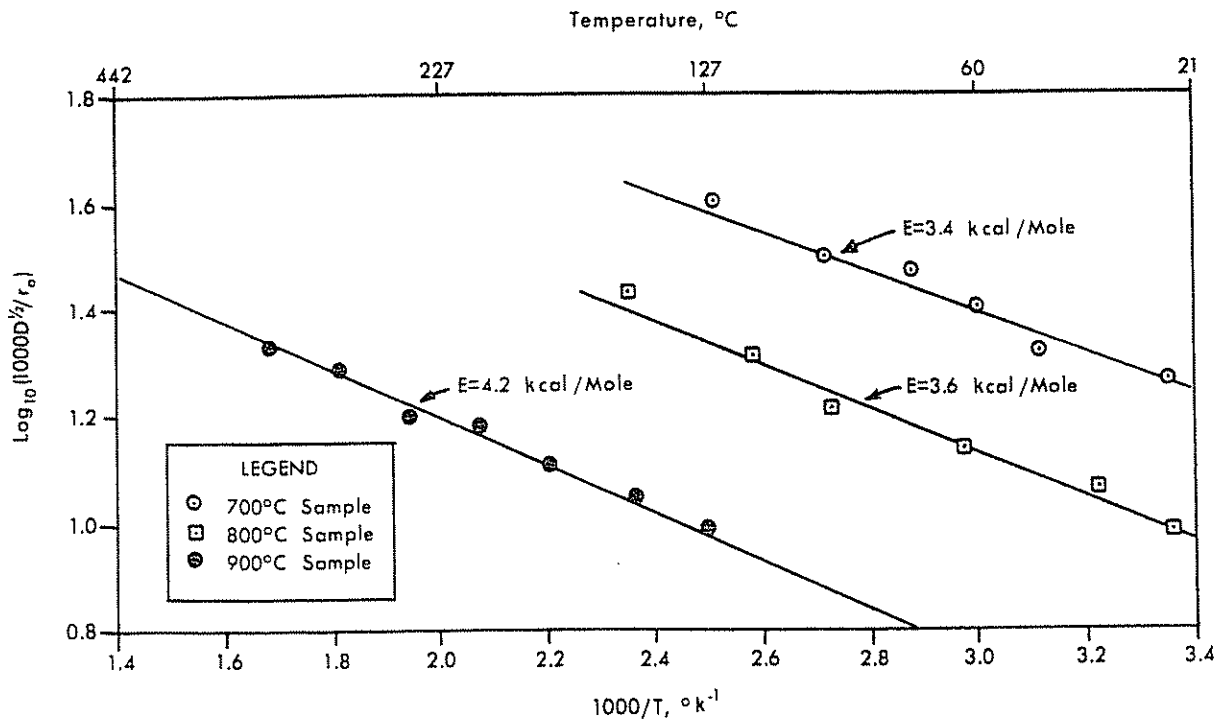


FIG. 5. Activation energy plots for the diffusion of argon from heat treated St. Nicholas anthracite.

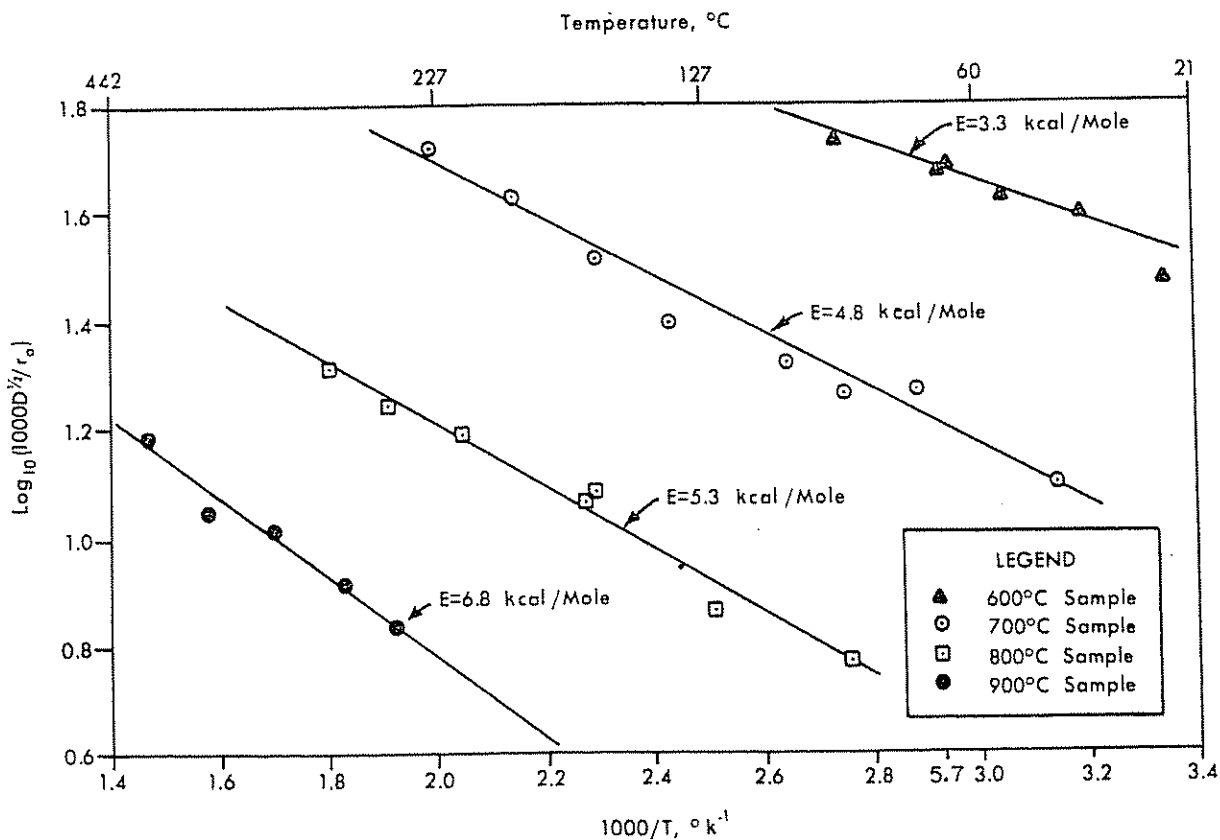


FIG. 6. Activation energy plots for the diffusion of argon from heat treated Dorrance anthracite.

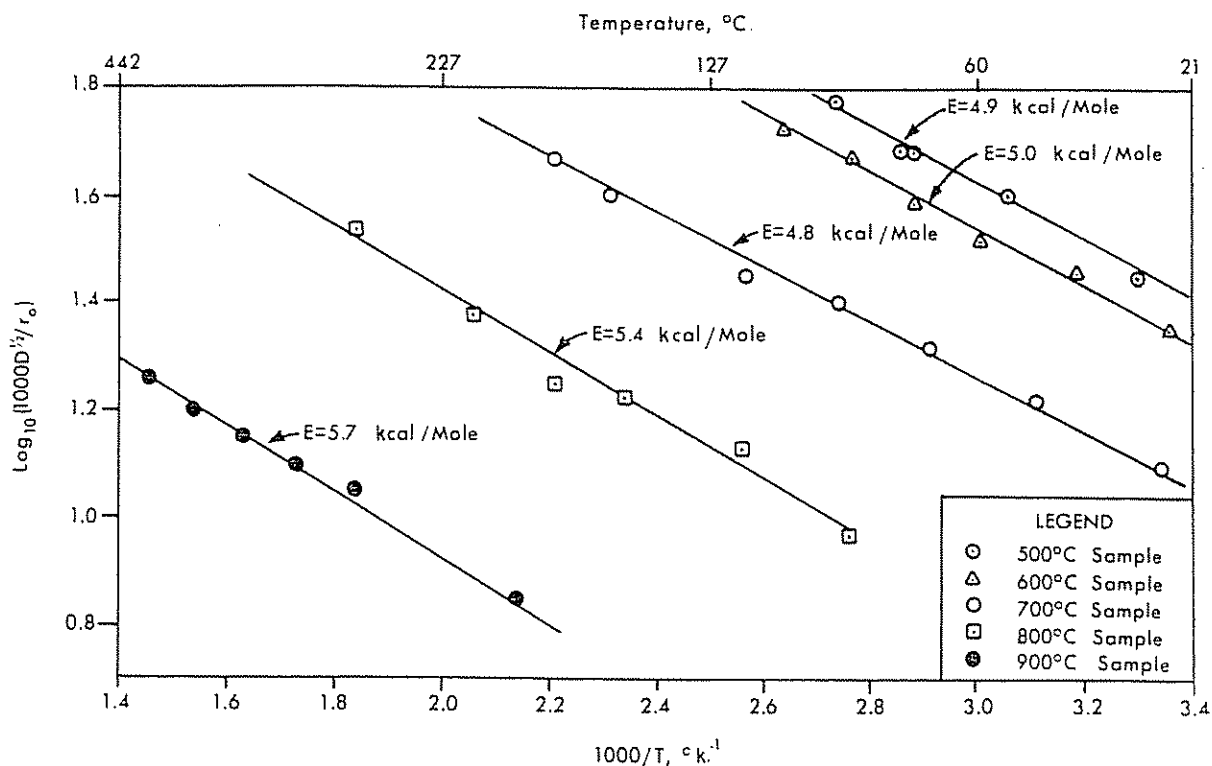


FIG. 7. Activation energy plots for the diffusion of argon from heat treated Treverton anthracite.

Treverton samples heat treated up to 900°C. Again, increases in the activation energy for diffusion occurred with increasing HTT. It is of interest, however, that the Dorrance anthracite showed a greater increase in activation energy for argon diffusion than did Treverton or St. Nicholas. Further, the activation energy for the diffusion of argon from Treverton was appreciably higher than the values for the other anthracites, when the samples were heated only to 600°C. Since nitrogen has a kinetic dimension close to that of argon (3.41 Å), this is consistent with the fact that the nitrogen surface area of Treverton heat treated to 600°C was considerably less than the nitrogen area of the Dorrance sample.

#### 4. CONCLUSIONS

Heat treatment of Pennsylvania anthracites in an oxygen-free atmosphere above *ca.* 700°C is seen to decrease the average size of the ultrafine pores. The result is a sharp decrease in total surface area, as measured by carbon dioxide adsorption, for HTT at or above 900°C and a continuous increase in the activation energy for diffusion of gases from the ultrafine pores with increasing HTT.

*Acknowledgement*—We appreciate the financial support of the Coal Research Board of the Commonwealth of Pennsylvania which made this work possible.

#### REFERENCES

1. KINI K. A., NANDI S. P., SHARMA J. N., Iyengar M. S. and LAHIRI A., *Fuel* **35**, 71 (1956).
2. WALKER P. L. JR. and GELLER I., *Nature* **178**, 1001 (1956).
3. ANDERSON R. B., HALL W. K., LECKY J. A. and STEIN K. C., *J. Phys. Chem.* **60**, 1548 (1956).
4. JOY A. S., *Conference on Science in the Use of Coal*, pp. A-67 to A71. Institute of Fuel (1958).
5. GREGG S. J. and POPE M. I., *Fuel* **38**, 501 (1959).
6. METCALFE J. E. III, KAWAHATA M. and WALKER P. L. JR., *Fuel* **42**, 233 (1963).
7. EMMETT P. H., A.S.T.M. Tech. Publ., pp. 95-105, No. 51 (1941).
8. KOTLENSKY M. V., Ph. D. Thesis. The Pennsylvania State University (1959).
9. WALKER P. L. JR., RUSINKO F. JR. and RAATS E., *J. Phys. Chem.* **59**, 245 (1955).
10. SCHERRER P., *Nachr. Ges. Wiss. Göttingen* **2**, 98 (1918).
11. SHORT M. A. and WALKER P. L. JR., *Carbon* **1**, 3 (1963).
12. NELSON E. T. and WALKER P. L. JR., *J. Appl. Chem.* **11**, 358 (1961).

13. NELSON E. T., YOUNG G. J. and WALKER P. L. JR., Special Research Report No. 3. Coal Research Board, Commonwealth of Pennsylvania (1958).
14. WORRALL J. and WALKER P. L. JR., Special Research Report No. 16. Coal Research Board, Commonwealth of Pennsylvania (1959).
15. WALKER P. L. JR., RUSINKO F. JR. and AUSTIN L. G., *Advances in Catalysis* **11**, 133 (1959).
16. ANDERSON R. B., HOFER L. J. E. and BAYER J., *Fuel* **41**, 559 (1962).
17. WALKER P. L. JR., *Amer. Scientist* **50**, 259 (1962).
18. GIBSON J., HOLOHAN M. and RILEY H. L., *J. Chem. Soc.* 456 (1946).
19. KINNEY C. R., NUNN R. C. and WALKER P. L. JR., *Ind. Eng. Chem.* **49**, 880 (1957).
20. WALKER P. L. JR., RUSINKO F. JR., RAKSZAWSKI J. F. and LIGGETT L. M., *Proceedings of the Third Carbon Conference*, p. 643. Pergamon Press, Oxford (1958).
21. WALKER P. L. JR., GARDNER R. P., SHORT M. A. and AUSTIN L. G., *Proceedings of the Fifth Carbon Conference*, Vol. 2, p. 483. Pergamon Press, Oxford (1963).
22. KINGTON G. L. and LAING W., *Trans. Faraday Soc.* **51**, 287 (1955).
23. HIRSCHFELDER J. O., CURTISS C. F. and BIRD R. B., *Molecular Theory of Gases and Liquids*, p. 1110. John Wiley, New York (1954).
24. NANDI S. P., Ph. D. Thesis. The Pennsylvania State University (1964).