

Diffusion studies of porous materials

Part 2 *Effects of thermal and radiolytic oxidation on the pore structure of a "high-reactivity" nuclear graphite*

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Measurements of transient diffusion phenomena are reported for a "high-reactivity", 20% open-pore volume (OPV), nuclear graphite, in the virgin state and after thermal oxidation in air or radiolytic oxidation in a carbon dioxide/carbon monoxide/methane coolant mixture. The volume of restricted access pores (RAPs) in this graphite is small (< 5% of the OPV) and the changes in pore structure with oxidation are in general very similar for thermal and radiolytic oxidation. A significant difference is that the RAP volume decreased (as expected) on slow thermal oxidation, but showed a slight increase during radiolytic oxidation. This is consistent with a model in which the methane is severely depleted in RAPs, which are therefore subject to an effectively uninhibited corrosion.

1. Introduction

In Part 1 [1] a technique was described for studying the pore structure of porous materials by measuring the transient diffusion of a tracer gas from the pores. A particular feature of this non-steady-state technique is its ability to provide information on "ink-bottle" or "restricted-access" pores (RAPs) which have no effect on steady-state gas transport but which may be very important to the application of porous materials in dynamic applications. One important example is the moderator graphite used in gas-cooled nuclear reactors, such as the advanced gas-cooled reactors (AGRs) used in the present British nuclear power stations. This is a porous material with a complex pore structure arising from its manufacture from coke particles (grist) and some form of pitch. The grist particles are themselves porous and the process of binding and graphitizing these creates a system of larger interlinking pores. Finally the whole structure may be modified by a series of impregnations and bakings before the final graphitization. The complex nature of the graphite pore structure has been elegantly revealed by optical and electron microscopic studies of graphites and gold casts of the pore structures [2, 3].

It is a significant technological problem of the

AGR that the carbon dioxide coolant, under irradiation, attacks the graphite to form carbon monoxide, with a consequent loss of moderator which must be kept within acceptable bounds. The carbon monoxide itself has a retarding effect on the reaction, but methane is a more effective inhibitor and is added to reactor coolants to reduce the loss of graphite. The methane itself is consumed in the radiolytic processes and since the reactions take place predominantly within the graphite pores, the relevant gas concentrations near the solid surface are determined by a complex interplay of the chemical processes with diffusion of reactants into, and products out of, the pore structure. As a result the methane level can be seriously depleted inside the graphite and since the bulk coolant methane concentration has to be restricted because of carbon deposition at high concentrations, a detailed understanding of these systems is required to ensure that the graphite can be adequately protected. The chemistry and technology of these problems have been reviewed [4, 5].

More specifically, attention has been drawn [3, 6, 7] to the possible significance of RAPs in the reactor graphite. Pores having a large volume behind a narrow neck could suffer a particularly

marked depletion in the methane level and oxidation might proceed rapidly inside such pores, even though the bulk methane concentration is such as to provide adequate protection. We are therefore applying transient and steady-state diffusion methods to investigate the pore-structure of moderator graphite and its evolution as the materials are modified by oxidative weight-loss. This paper describes the results obtained for a "high-reactivity" open-pored graphite, and a later paper will deal with a higher-density material typical of that used in the AGRs.

2. Experimental procedure

The apparatus used for transient diffusion measurements was essentially as described previously [1], except that the whole of the valve and pipework is now thermostatted along with the FID. The system has also been extended to permit the measurement of steady-state diffusivity using a sample holder of the type shown in Fig. 1. The steady-state flow of tracer gas through the specimen was measured at a series of differential pressures (recorded by an SE Laboratories differential transducer type SE180/5 PSI with SE905 converter connected to a digital meter, sensitive to about 10 Pa). A typical plot of tracer flow against pressure difference is shown in Fig. 2; the diffusivity was calculated from the flow at zero pressure difference, and permeability data can be extracted from the slope and curvature of the plot. After the measurement of diffusivity, one face of the specimen was blanked off by a plate sealed with epoxy resin and the sample mounted as described previously [1] for the transient diffusion measurements.

The graphite used in these experiments was an extruded petroleum pitch coke graphite of French

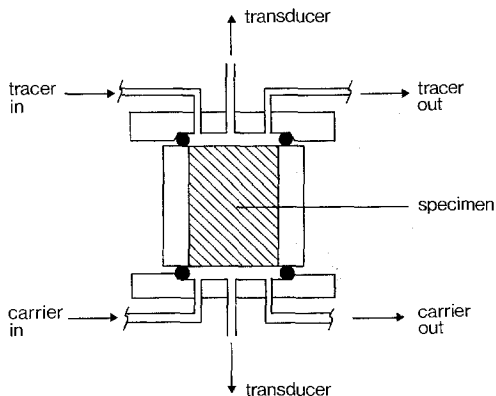


Figure 1 Sample holder for steady-state measurements.

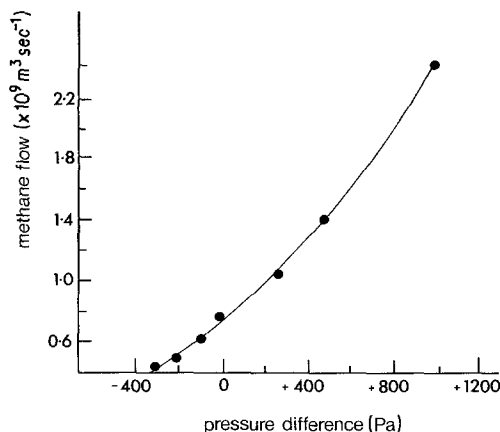


Figure 2 Illustrative plot of steady-state methane flow versus pressure difference (6.52 wt% loss thermally oxidized specimen).

manufacture, having a relatively high chemical reactivity and an open pore volume (OPV) of about 20%. We expect to report later on measurements involving the higher density graphites common in British reactors. Samples of the virgin graphite were supplied by UKAEA (Springfields Nuclear Power Development Laboratory), together with two samples which had been radiolytically oxidized in a carbon dioxide/carbon monoxide/methane coolant in the Anglo-French BFB loop at Grenoble [8–11]. The steady-state pore-structure parameters supplied by SNPDL are given in Table I.

A series of the virgin samples (from a different block) was thermally oxidized in a small current of air for 151 days at approximately 425°C at Manchester Polytechnic, under which conditions the oxidation should have been essentially homogeneous. A "diffusion length" can be calculated as $(\lambda D/k)^{1/2}$, where λ and D are as defined later, and k is the first-order volume rate constant for removal of oxygen; this was 6 cm even for the worst case, well in excess of the specimen dimensions. Nevertheless, the samples showed significant reductions in diameter, and mass measurements after successive machining revealed a much faster oxidation at the surface than in the "core" (Table II). This phenomenon (which has been observed previously [12]) is certainly not due to diffusional control of the reaction and may be attributed to the machining of the curved surface, either depositing metallic impurities which enhance the reaction rate [13–15], or generating crystal defects at which oxidation occurs preferentially [16–19]. The main point for the present purposes is that the machined "core" specimens were shown

TABLE I Steady-state parameters measured at SNPDL

Graphite	OPV, ϵ	CPV	Diffusivity, λ	Permeability coefficients	
				$10^{13} B_0$ (m ²)	$10^3 K_0$ (m)
Virgin*	0.210	0.047	0.0027	0.246	1.79
9.77% RO†	0.316	0.031	0.0060	0.577	2.51
22.6% RO†	0.415	0.009	0.0249	0.542	3.08

*Average of several samples from block used for radiolytically oxidized (RO) specimens.

†% RO ≡ Per cent weight loss during radiolytic oxidation.

by the differential machining to be essentially homogeneous.

Both steady-state and transient diffusion measurements were made on each of the specimens. Typical results are shown graphically in Figs 2 to 4, and the analysis of these is discussed in the following sections.

3. Theory

The present results are interpreted in terms of a mathematical treatment based on that of Goodknight *et al.* (GKF) [20]. These workers considered one-dimensional diffusion in a sample containing both transport pores (TPs) and dead-ended pores (RAPs), the latter having a single uniform time constant. The differential equations for such a system are Equations 1 and 2 and GKF solved these to obtain an infinite series expression for $c_1(x, t)$. A straightforward extension of their approach leads to expressions for $c_2(x, t)$, the total tracer left in the sample at time t , and most pertinently to the present work, Equation 3 for the rate of flow of tracer out of the specimen at time t .

$$\frac{\partial c_1}{\partial t} = \frac{\lambda D}{\phi_1} \frac{\partial^2 c_1}{\partial x^2} - \frac{\phi_2}{\phi_1} \frac{\partial c_2}{\partial t} \quad (1)$$

$$\frac{\partial c_2}{\partial t} = Y_2(c_1 - c_2) \quad (2)$$

where $c_1(x, t)$ is the concentration of tracer in transport pores at position x and time t ; $c_2(x, t)$ is the concentration of tracer in RAPs at x, t ; D is the free-gas diffusion coefficient; λ is the diffusivity of material (ratio of effective diffusion coefficient

to D); ϕ_1 is the fractional TP volume; ϕ_2 is the fractional RAP volume; Y_2 is the reciprocal time constant for RAPs (e.g., for a simple RAP with volume V , neck area a and neck length l , $Y_2 = Da/Vl$).

Then the rate of elution of tracer from unit cross-sectional area of sample at time t , $f(t)$ is given by

$$f(t) = (\lambda D c_0 / L) \sum_{i=1}^{\infty} \beta_i [\exp(S_i^+ t) / (S_i^+ Z_i^+) + \exp(S_i^- t) / (S_i^- Z_i^-)] \quad (3)$$

where c_0 is the initial tracer concentration (volume-fraction), L is the sample length,

$$S_i^{\pm} = \frac{1}{2} [-B_i \pm (B_i^2 - 4Y_2 \lambda D \beta_i^2 / \phi_1)^{\frac{1}{2}}] \quad (4)$$

$$Z_i^{\pm} = (\partial S_i^{\pm} / \partial \beta_i)^{-1} \quad (5)$$

$$\beta_i = \pi(i - \frac{1}{2}) / L \quad (6)$$

$$B_i = Y_2(1 + \phi_2 / \phi_1) + \lambda D \beta_i^2 / \phi_1 = Y_2(1 + \phi_2 / \phi_1) + Y_1(i - \frac{1}{2})^2 \quad (7)$$

and $Y_1 = \lambda D \pi^2 / \phi_1 L^2$ (Y_1 is the reciprocal time-constant for the TP system). (8)

Now Y_1 decreases as L increases and for the systems under consideration, the parameters are such that $Y_2 / Y_1 \ll 1$ (e.g., 0.02) and this enables simplifying approximations to be made, giving

$$S_i^- \approx -Y_2, \quad (9)$$

$$Z_i^- \approx -\phi_1 Y_1 \pi(i - \frac{1}{2})^3 / 2\phi_2 Y_2^2 L, \quad (10)$$

$$S_i^+ \approx -Y_1(i - \frac{1}{2})^2 \quad (11)$$

and $Z_i^+ \approx -\pi / 2 Y_1 (i - \frac{1}{2}) L. \quad (12)$

TABLE II Illustrative data for thermal oxidation

Diameter (mm)			Weight loss (%)	
Initial specimen	After oxidation	"Core" after machining	Overall	"Core"
12.10	12.01	8.06	5.15	2.95
12.85	12.71	8.10	10.32	6.53
11.80	11.60	8.11	16.53	8.32

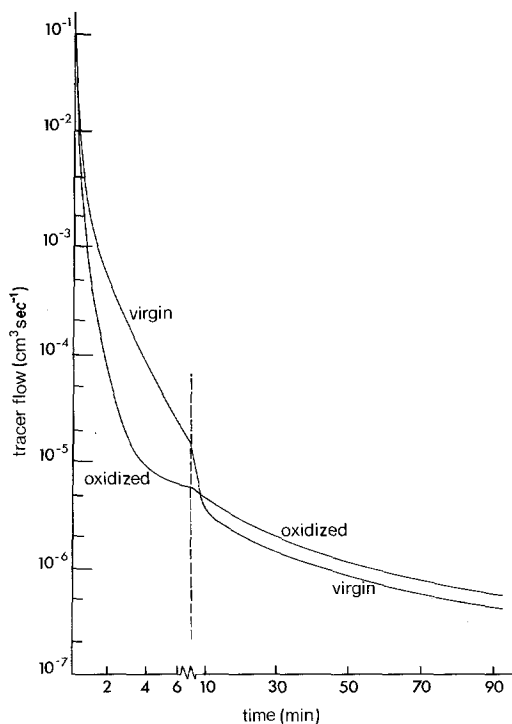


Figure 3 Transient diffusion results for virgin and radiolytically oxidized (22.6 wt% loss) samples (specimen length 1.1 cm).

The elution equation (Equation 3) is then found to split into two distinct sections, Equation 13, corresponding to rapid emptying of the TPs, followed by much slower diffusion from the RAPs.

$$f(t) = \left(\frac{2\lambda D c_0}{L} \right) g [\exp(-Y_1 t)] + \left(\frac{\phi_2 Y_2 c_0}{L} \right) \exp(-Y_2 t) \quad (13)$$

The first term in Equation 13 is simply the expression for diffusion from uniform capillaries [21], and the second term represents diffusion from the RAPs. Under these circumstances, the concentration in the TPs is always much smaller than that in RAPs and there will be no interaction between RAPs with different time constants. A series of terms can therefore be included for different RAPs. Finally, tracer gas in the dead-space of the apparatus complicates the experimental traces and can be simulated by a simple exponential function. We therefore arrive at

$$f(t) = V_D \exp(-Y_D t) + f_1 g [\exp(-Y_1 t)]$$

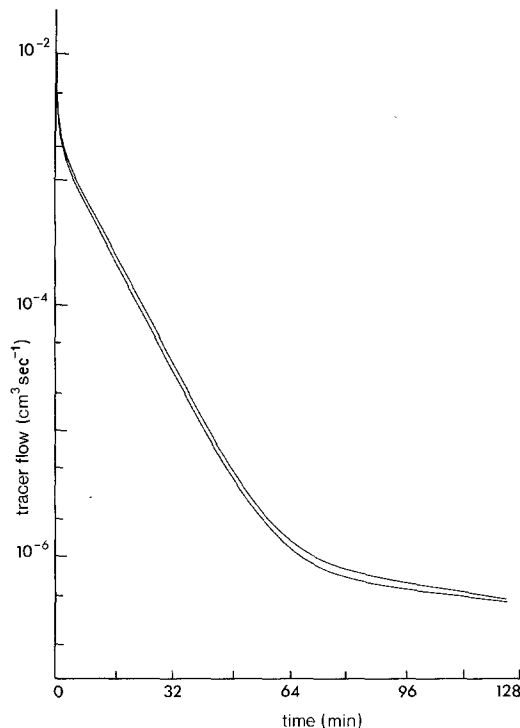


Figure 4 Duplicate transient diffusion runs for thermally oxidized specimen (6.52 wt% loss, specimen length 4.0 cm).

$$+ \sum_{i=2}^{n+1} f_i \exp(-Y_i t), \quad (14)$$

where V_D is the total volume in dead-space, Y_D is the reciprocal time-constant for dead-space, n is the number of distinct RAP types,

$$g(x) = \sum_{i=1}^{\infty} x^{(i-\frac{1}{2})^2}$$

and the coefficients f_i are given by

$$f_1 = 2\lambda D c_0 / L \quad (15)$$

and

$$f_i = \phi_i Y_i c_0 / L \quad (i = 2 \dots) \quad (16)$$

where ϕ_i and Y_i are the fractional volume and reciprocal time constant of RAPs, i .

Equation 14 was fitted to the experimental results using the least-squares minimization method of Peckham [22]. The function minimized, $s(x)$, is given by

$$s(x) = \sum_{i=1}^m [\ln F(t) - \ln f(t)]^2, \quad (17)$$

where $F(t)$ is the experimental flow at t , $f(t)$ is the theoretical flow from Equation 14, m is the number of experimental points plotted, and x

contains the parameters of Equation 14, i.e., V_D , Y_D and f_i , Y_i (for $i = 1$ to $n + 1$).

The required pore-structure parameters are easily calculated from the optimized components of x , using Equations 15 and 16. Two further parameters were also calculated from the results; the tortuosity, τ , is defined as the ratio of the apparent length of the TPs to the actual sample length,

$$\tau = (\phi_1/\lambda)^{\frac{1}{2}}, \quad (18)$$

and the apparent fractional cross-sectional area, α , of the TPs is defined such that when multiplied by their apparent length, it gives the OPV ϕ_1 in the TPs,

$$\alpha = (\phi_1 \lambda)^{\frac{1}{2}}. \quad (19)$$

The TP system can thus be modelled in some respects as a series of cylindrical pores of length τL and cross-sectional area α .

4. Results and discussion

The parameters extracted from the steady-state and transient diffusion experiments are presented in Table III. It is immediately apparent from Figs 3 and 4 and Table III, that the volume of RAPs in all these samples is small (fractional OPV in RAPs is in general < 0.01 , or $< 5\%$ of the total OPV). Under these circumstances the parameter values obtained are sensitive to very small variations in the experimental data and the precise numerical values are probably not highly reliable, even though reproducibility was fairly good (e.g. Fig. 4) and a sophisticated error analysis indicated that the standard errors of the derived parameters were in general a small fraction of their values. Comparisons are also complicated by several differences between the experiments with the thermally oxidized (TO) and radiolytically oxidized (RO) specimens. Firstly, the samples available to us were cut from different graphite blocks, so that the inherent variability within a block is enhanced for comparison between the two series. Secondly, the RO samples were shorter than the TO samples (for reasons connected with the irradiation facility) and thirdly, the measurements were made approximately eighteen months apart, during which time the experimental technique had developed significantly. Although the block and length effects are not considered substantial (see below), we nevertheless do not feel that significance can be attached to the fact that the thermally oxidized specimens could be satisfactorily modelled with

only one RAP type, whereas the inclusion of two RAP sizes gave improved fits for the radiolytically oxidized series. Rather, the total RAP volume is considered to be the significant parameter in this respect. Another significant problem arose from the small sample sizes and the rates of elution from the transport pores in this open-structured graphite, especially after oxidation. Under these circumstances it is difficult to separate accurately the contribution of the sample-holder dead-space from that of the TPs (both 0.1 to 0.5 cm³). There is thus considered to be satisfactory agreement between the total OPV found from the transients ($\phi_1 + \phi_2 + \phi_3$) and the helium pyknometer values where these are available (Table I) (0.204, 0.313, 0.487, cf. 0.210, 0.316, 0.415, respectively). The diffusivity from the transient results is similarly subject to uncertainty from the same source and it is doubtful whether any significance can be attached to a comparison of the transient and steady-state λ values. There is no fundamental reason why these should be identical for a complex pore structure, but the present data do not give strong indications of a real difference.

It is instructive to compare the results for the virgin specimens of different lengths. By definition the slope Y_1 of the transport pore section of the elution curve should vary as D/L^2 , i.e., it should be 13.2 times greater for the TO control specimens than for the RO control specimens. The experimental factor is 13.1, in excellent agreement despite the order of magnitude difference in the elution times involved. This agreement provides strong grounds for believing that the virgin samples from the two blocks are very similar in their properties and that the GKF-based theory is indeed applicable to this type of material.

Fig. 5 shows the development of the various pore structure parameters with oxidation in the two series of results. The major changes on oxidation are very similar for thermal and radiolytic oxidation, namely, the expected increases in diffusivity, transport pore volume and apparent pore area, and the accompanying decrease in tortuosity. This similarity is perhaps not surprising for an open-structured graphite, which would be expected to oxidize fairly uniformly throughout the TP system under most conditions. The present work was aimed particularly at investigating the behaviour of restricted area pores, and although the volume of these pores is so small as to make their study difficult, some tentative conclusions can be

TABLE III Pore-structure parameters extracted from diffusion results

Weight loss (%)*	Length (cm)	Diameter (cm)	Transport pore parameters			Restricted access pore parameters						
			λ^{\ddagger}	λ	ϕ_1	τ	α	ϕ_2	$10^4 Y_2$ (sec ⁻¹)	ϕ_3	$10^4 Y_3$ (sec ⁻¹)	$\phi_2 + \phi_3$
Virgin	3.96	0.81	0.0087	0.0045	0.152	5.8	0.026	—§	0.0187	2.5	0.0187	0.0187
2.95 TO	3.85	0.81	0.0191	0.0116	0.246	4.6	0.056	—	0.0032	1.7	0.0032	0.0032
3.40 TO	3.90	0.81	0.0216	0.0111	0.239	4.6	0.051	—	0.0024	2.3	0.0024	0.0024
6.52 TO	4.00	0.81	0.0261	0.0158	0.305	4.2	0.074	—	0.0022	1.3	0.0022	0.0022
8.32 TO	3.90	0.81	0.0300	0.0203	0.303	3.9	0.078	—	0.0016	2.5	0.0016	0.0016
Virgin	1.08	0.78	0.0027	0.0056	0.179	5.8	0.031	0.0031	0.0070	3.3	0.0070	0.0101
Virgin	1.08	0.78	0.0027	0.0070	0.208	5.5	0.037	0.0049	0.0046	4.5	0.0046	0.0095
9.77 RO†	1.14	0.78	0.006	0.016	0.286	4.3	0.067	0.0038	0.0065	4.9	0.0065	0.0103
9.77 RO†	1.14	0.78	0.006	0.018	0.318	4.3	0.074	0.0044	0.0063	3.4	0.0063	0.0107
22.6 RO	1.14	0.78	0.025	0.051	0.474	3.1	0.151	0.0040	0.0084	2.9	0.0084	0.0124

*TO = thermally oxidized, RO = radiolytically oxidized (see text for details).

†Duplicate runs on the same specimen.

‡Diffusivity from steady-state experiments; all other results from transient elution. Steady-state diffusivity results for radiolytically oxidized specimens provided by SNPDL for typical material. To samples measured (in duplicate) in the present work, on the same samples as used for transients.

§ Only one RAP size fitted; see text.

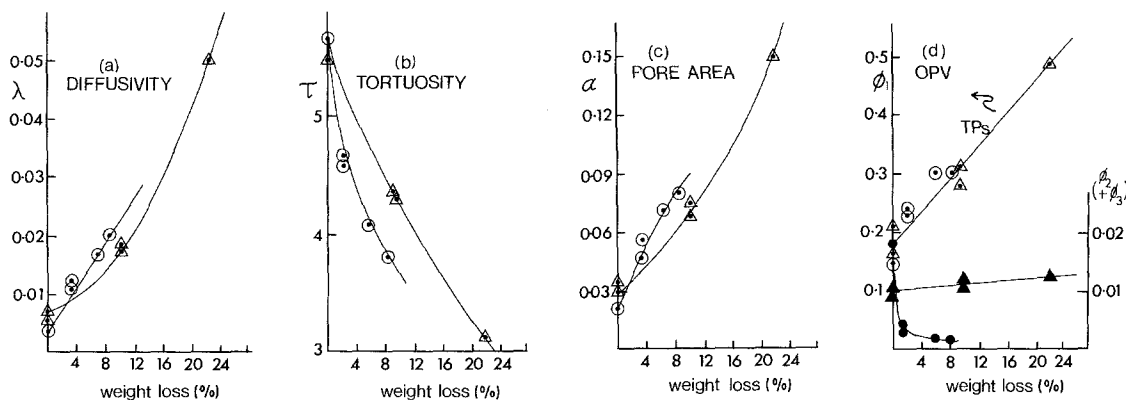


Figure 5 Pore structure parameters from transient elution results: \circ , \bullet = thermally oxidized; Δ , \blacktriangle = radiolytically oxidized.

drawn. Fig. 5d indicates that the RAP volume decreased markedly on thermal oxidation; this would be expected when oxidation occurs uniformly, since the RAP necks would be oxidized out and the RAPs would progressively become part of the TP system. In contrast, the data indicate a slight increase in RAP volume on radiolytic oxidation in the methane-inhibited coolant used. This would be consistent with a model [3, 6, 7] in which diffusion of methane into the RAPs is unable to maintain the inhibitor concentration at its nominal value in the face of radiolytic depletion of methane inside the RAPs. The RAPs would thus tend to corrode more rapidly in their interiors than at the necks and their volume would be increased to counteract the effect of the general opening-up which is simultaneously occurring. This model can be justified quantitatively [23] using the RAP time constants of $ca\ 2 \times 10^{-4}\ sec^{-1}$ from Table III and known data on $G(-CH_4)$ as a function of composition, e.g., [24, 25].

Similar experiments with an impregnated Gilso carbon graphite are in hand and will be reported later.

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References

- J. D. CLARK, C. S. GHANTHAN and P. J. ROBINSON, *J. Mater. Sci.* **14** (1979) 2937.
- R. LIND, Proceedings of the 4th London International Conference on Carbon and Graphite, London, September 1974 (Society of Chemical Industry, London, 1976) p. 445.
- J. V. SHENNAN, Conference on Gas Chemistry in Nuclear Reactors, Salford, April 1980, edited by A. Dyer (Heyden, London, 1980) p. 98.
- Proceedings of the 4th London International Conference on Carbon and Graphite, London, September 1974 (Society of Chemical Industry, London, 1976).
- A. DYER (Ed), Conference on Gas Chemistry in Nuclear Reactors, Salford, April 1980 (Heyden, London, 1980).
- A. BLANCHARD, *ibid.* p. 134.
- J. V. BEST, *ibid.* p. 141.
- P. CAMPION, A. BLANCHARD, R. LIND, R. J. BLANCHARD and C. KOCH, Proceedings of the 4th London International Conference on Carbon and Graphite, London, September, 1974 (Society of Chemical Industry, London, 1976) p. 452.
- P. CAMPION, R. LIND, R. J. BLANCHARD and C. KOCH, *ibid.* p. 459.
- A. BLANCHARD, J. KETCHEN, P. SCHOFIELD and P. CAMPION, Conference on Gas Chemistry in Nuclear Reactors, Salford, April 1980, edited by A. Dyer (Heyden, London, 1980) p. 129.
- P. CAMPION, A. BLANCHARD, J. KETCHEN and P. SCHOFIELD, 14th Biennial Conference on Carbon, Pennsylvania, June 1979, (American Chemical Society and the Pennsylvania State University, Pennsylvania, 1979) p. 449.
- A. BLANCHARD, private communication.
- P. L. WALKER, M. SHELEF and R. A. ANDERSON, *Chem. Phys. Carbon* **4** (1968) 287.
- F. S. FEATES, P. S. HARRIS and B. G. REUBEN, *J. Chem. Soc. Faraday I* **74** (1970) 2011.
- Idem*, Proceedings of the 4th International Conference on Carbon and Graphite, London, September 1974 (Society of Chemical Industry, London, 1976).
- J. G. BROWN, J. DOLLIMORE, C. M. FREDMAN and B. H. HARRISON, *Thermochim. Acta* **1** (1970) 499.
- G. R. HENNING, 5th Conference on Carbon, Pennsylvania, Vol. 1 (1963) p. 143.
- P. L. WALKER, R. N. LAINE and F. J. VASTOLA, *ibid.* Vol. 2 (1963) p. 211.
- R. J. GOOD, L. A. GINIFALCO and G. KRAUS, *J. Phys. Chem.* **62** (1958) 1418.
- R. C. GOODKNIGHT, W. A. KLIKOFF and

- I. FATT, *ibid.* **64** (1960) 1162. Note that a factor of 2 is erroneously missing from the denominator in the last line of Appendix I.
21. J. CRANK, "The Mathematics of Diffusion" 2nd edn (Oxford University Press, Oxford, 1975) p. 50.
22. G. PECKHAM, *Computer J.* **13** (1970) 418.
23. P. J. ROBINSON, to be published.
24. R. L. FAIRCLOTH, Conference on Gas Chemistry in Nuclear Reactors, Salford, April 1980, edited by A. Dyer (Heyden, London, 1980) p. 148.
25. J. A. PRITCHARD, P. C. MATTHEWS and J. E. M. PALMER, *ibid.* p. 239.

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