D varies only slightly with concentration in this range and can be taken as 1.474×10^{-5} cm.^{2}/sec.

Measured pore volumes, bulk lengths and D, when substituted into equation 2 gives $(dR_t/d\sqrt{t})_{calcd}$ for a system of open area q and length L_u. The observed values of $dR_t/d\sqrt{t}$ taken from Mysels and Stigter are for a system of open area q and length l_u where l_u is the actual fluid path length through the porous medium. The ratio $(dR_t/d\sqrt{t})_{calcd}/(dR_t/d\sqrt{t})_{obsd}$ is then a tortuosity, k_1, where $k_1 = l_u/L_u$.[5] The tortuosity so obtained should be characteristic of the pore geometry only. It gives the ratio of the length of fluid path through the porous disc to the bulk length of the disc.

The Mysels and Stigter solution of the transient diffusion equation is based on the assumption that the porous material is equivalent to a bundle or network of capillary tubes and that there are no dead end pores which can act as sources or sinks of diffusing material.

Columns 2 and 3 in Table I give the calculated and observed values of $dR_t/d\sqrt{t}$. Column 4 gives the tortuosity, k_1, calculated from these transient diffusion measurements.

TABLE I

COMPARISON OF TORTUOSITES FROM DIFFUSION AND CONDUCTANCE

1 Disc	2 $\left(\frac{dR_t}{d\sqrt{t}}\right)_{calcd}$	3 $\left(\frac{dR_t}{d\sqrt{t}}\right)_{obsd}$	4 k_1 (from diffusion)	5 k_1' (from conductance)
2 U	0.01765	0.01331	1.325	1.315
4 U	.02713	.02000	1.365	1.375
5 U	.02620	.01875	1.396	1.395
6 U	.02610	.01874	1.391	1.385

Many authors[6-8] have shown that the pore geometry characteristic called the tortuosity above can also be calculated from electrical resistance measurements on a porous material saturated with a conducting fluid. The relation is

$$k_1' = \sqrt{\frac{rV}{\rho L^2}} \qquad (3)$$

where r is the measured resistance of a porous body of pore volume V, length L, and saturated with a fluid of specific resistance ρ. Equation 3 is also based on a model of a porous medium that does not include dead end pore space.

If the tortuosities calculated from transient diffusion and electrical resistance measurements on a given porous material are the same then there is no dead end pore volume or not enough to influence transient diffusion. This must be true because dead end pore volume will not have the same effect on tortuosities calculated from transient diffusion and electrical resistance.

The porous discs listed in Table I were saturated with sodium chloride solution for which $\rho = 257$ ohm cm. at 23°. For this solution, about 0.05 M, in porous glass the surface conductance has been shown to be less than one per cent. of the total conductance.[8] The resistance of the saturated discs was measured between gold-plated brass electrodes by use of a conductance bridge operating at 1000 c.p.s. An electrolyte-saturated piece of blotting paper was placed between the discs and the electrodes to ensure contact. The resistance of the two saturated pieces of blotting paper alone was also measured. This resistance was subtracted from the total to give the resistance of the porous disc. The resistance of the paper was 5% of the total and could be reproduced to ±5%. The uncertainty in the resistance of the porous disc introduced by use of the blotting paper as contact material was no greater than 0.25%. The total uncertainty in the resistance is probably 0.5%.

Column 5 of Table I gives k_1' calculated from resistance measurements by use of equation 3.

The tortuosities given in columns 4 and 5 are identical within the precision of the measurements. This can be taken to mean that the tortuosity of sintered porous glass is the same in transient diffusion as in electrical conductance.

Schofield and Dakshinamurti[6] already have shown that the tortuosity of a given porous material is the same in steady state diffusion and electrical conductance. Their conclusion means simply that Fick's first law of diffusion and Ohm's law for a porous body are analogous. The conclusion drawn here, that for sintered porous glass the tortuosity is the same in transient diffusion and electrical conductance, is more significant. It indicates that Fick's second law of diffusion, when applied to sintered porous glass, has no source function and can be integrated directly to give Fick's first law which is in turn analogous to Ohm's law. That is, $G(x,t) = 0$ in

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} + G(x,t) \qquad (4)$$

where $G(x,t)$ is the strength of the source or sink in unidimensional diffusion. A dead end pore can act as a source or sink because it can add or subtract from the transient diffusion flux. If $G(x,t) = 0$ for sintered glass then there are no dead end pores in this material or at least none which can influence transient diffusion of the kind carried out by Mysels and Stigter.[3,4]

Studies are now under way in this Laboratory to evaluate the effect of dead end pores on transient diffusion.

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(5) This is not the same tortuosity used by Barrer[1] and Wyllie and Rose.[2] Their tortuosity is equal to k_1^2. The difference lies in the use here of an open cross-sectional area equal to V_u/L_u whereas Barrer, Wyllie and Rose, and others have used V_u/l_u.

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γ-RADIOLYSIS OF ETHYLENE

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It appears that the gaseous products formation in γ-radiolysis of ethylene has not been investigated.[1]

We have studied the problem and summarize our results in this note.

Experimental

Matheson C. P. grade ethylene and Matheson nitric oxide (min. 99%) were degassed by freeze-pump technique and subjected to bulb-to-bulb distillation on a vacuum line. The only detectable impurities in the purified gases were 0.007% ethane in ethylene and 0.3% nitrous oxide in nitric oxide. The irradiation vessel was made of Pyrex glass and equipped with break-off seal and capillary constriction at opposite ends. Four fuel elements from a Materials Testing Reactor, shielded by 5.5 meters of water, were used as an irradiation source. All experimental data were obtained at 22.5 ± 1° (the temperature of pool water). Gamma field intensity was obtained by ionization-chamber technique, calibrated with a cerious-ceric chemical dosimeter.[2] Ionization chamber readings before and after each run were averaged. In a week of irradiation the γ-field intensity decreased 14%. After irradiations, gaseous products were analyzed by gas-liquid partition chromatography.

Results and Discussion

Gamma irradiation of ethylene yielded H_2, CH_4, C_2H_2, C_2H_6 and n-C_4H_{10} as gaseous products,[3] with G-values independent of energy input rate. G-values were also independent of initial ethylene pressure (Table I) and surface-to-volume ratio of the glass reactors (Table II). In order to identify the presence of free radicals, nitric oxide was added to a standard run. The results summarized in Table III show that the formation of ethane was completely inhibited by the presence of 5% nitric oxide. In electron bombardment of ethylene,[4] hydrogen atoms and methyl radicals are formed by direct detachment and by ion–molecule reactions. Similar reactions could occur in γ-radiolysis. Hence, ethane probably is formed by free radical reactions, such as

$$H + C_2H_4 \longrightarrow C_2H_5$$
$$C_2H_5 + H \longrightarrow C_2H_6$$

and

$$CH_3 + CH_3 \longrightarrow C_2H_6$$

The G-values for hydrogen, acetylene and n-butane were not affected by nitric oxide. This suggests that the reactions resulting in these products do not involve free radicals.

Table I

G-Values of Gaseous Products in γ-Irradiation of Ethylene at Different Ethylene Pressures

Energy input rate: 2 × 10^{19} e.v./g. hr.

Ethylene pressure (cm.)	G (molecules per 100 e.v.) C_2H_2	H_2	CH_4	C_2H_6	n-C_4H_{10}
120.0	3.2	1.9	0.05	0.56	0.48
99.8	3.0	1.8	[a]	.48	.45
80.0	3.7	2.0	.04	.59	[a]
60.0	3.7	2.0	.06	.67	.89
40.0	3.9	2.0	.10	.85	.89

[a] G-value not measured.

Table II

Effect of Glass Surface Upon the Gaseous Products Formation in the γ-Radiolysis of Ethylene

Ethylene pressure, 120 cm.; energy input rate, 2 × 10^{19} e.v./g. hr.

Surface area, vol. cm.$^{-1}$	G (molecules per 100 e.v.) C_2H_2	H_2	CH_4	C_2H_6	n-C_4H_{10}
0.8	3.6	2.2	0.06	0.36	0.30
5.7[a]	3.2	1.9	.05	.56	.48

[a] Packed with glass beads (4 mm. in diameter).

Table III

Effect of Nitric Oxide on the Gaseous Products in the γ-Irradiation of Ethylene[a]

Ethylene pressure, 100 cm.; energy input rate, 2 × 10^{19} e.v./g. hr.

Nitric oxide pressure (cm.)	G (molecules per 100 e.v.) C_2H_2	H_2	C_2H_6	n-C_4H_6
0.0	3.0	1.8	0.48	0.45
5.0	3.6	1.8	.00	[b]
10.0	3.9	1.7	.00	.40
20.0	4.1	1.9	.00	.37
30.0	4.1	1.7	.00	.41

[a] Due to the overlap of methane and nitric oxide peaks in chromatographs using silica gel columns, the effect of nitric oxide on the G-value for methane was not obtained. [b] G-value not measured.

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MISCIBILITY RELATIONS OF LIQUID HYDROGEN CYANIDE

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Published miscibility relations of hydrogen cyanide are meager, perhaps because of its toxicity. Several handbooks indicate complete miscibility with water or alcohol; and distribution at low concentrations is reported[1-6] between benzene and water or aqueous solutions. Freezing curves of four binary systems of hydrogen cyanide have been observed.[6-8] Its unique structure suggested studies of binary and ternary solubilities.

Hydrogen cyanide was distilled from a cylinder and condensed in a large tube in an ice-bath. It was kept at 0° (its b.p. is 26°) in a glass stoppered vessel. All operations were conducted in a hood, and no odor of cyanide was noted during the investigation.

Samples of hydrogen cyanide were taken by a 1-ml. graduated pipet connected to a "propipette,"[9] and mixed with other liquids in a small graduated glass stoppered tube which could be shaken for equilibrium studies. In view of the small samples,

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