Letters to the Editor

siderable information on the potential surfaces involved.

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Fractal chemical kinetics: Simulations and experiments

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An important class of heterogeneous chemical reactions occurs on or inside media that may have fractal structures. Examples are porous glasses,\textsuperscript{1} diffusion-limited aggregates\textsuperscript{2} and percolation clusters.\textsuperscript{3} Diffusion in or on such media is anomalous\textsuperscript{4–9} and so are diffusion-limited chemical reactions.\textsuperscript{10–22} What are the rules for transient and steady state reactions on such media? It has been shown experimentally,\textsuperscript{12,13} that an elementary reaction

\[ 2A\rightarrow\text{products} \] (1)

may have a reaction rate \( \rho = \text{density of species A}, \) \( t = \text{time} \):\n
\[ -dp/dt = kp^x \quad X > 2, \] (2)

where the power ("order") \( X \) may be much larger than 2. We present here a simple argument, relating \( X \) to the fractal dimension of random walks in a heterogeneous medium.\textsuperscript{5–9,22} For a spectral dimension \( d_s < 2 \) we find \( X = 1 + 2/d_s \). An amusing special case is a linear lattice, for which \( X = 3 \). The scaling result is validated by a very large scale Monte Carlo simulation on a supercomputer and by experimental results.

The random walker's exploration space \( S \) ("mean number of distinct sites visited") is given by

\[ S \propto t^f \quad 0 < f < 1 \quad (t \to \infty) \] (3)

where \( f = 1 \) for classical (3D homogeneous) diffusion and \( f < 1 \) for anomalous diffusion.\textsuperscript{6–8} It has been shown\textsuperscript{24} for the fractal exponent \( f \) that \( f = d_s/2 \) for \( d_s < 2 \). It has also been shown\textsuperscript{14,18,21} that the rate for the simple binary reaction (1) is

\[ -dp/dt = k_0 t^{-h} \rho^2 \quad 1 > h > 0 \quad (t \to \infty) \] (4)

where the heterogeneity exponent \( h \) is related to the fractal exponent \( f \). For the simple binary reaction of Eq. (1), \( h = 1 - f \). This has been verified by extensive simulations.\textsuperscript{21,22,25,26} The integrated rate equation, obtained from Eq. (4), is

\[ \rho^{-1} \rho^{-1} = k_0 f^{-1} t^{-f} \quad (f = 1 - f) \] (5)

where \( \rho = \rho(t = 0) \). Hence,\textsuperscript{14,20}

\[ t = (k_0 f^{-1}) t^{-1/\rho} \quad t \to \infty \quad \text{or} \quad \rho \to 0. \] (5')

A simple substitution of Eq. (5') into Eq. (4) gives \( k = k_0 f^{-1} t^{-1/\rho} \).

![FIG. 1. Effective reaction order \( X \) vs the mean steady state walker density, \( \text{CONC} = \langle \rho_s \rangle = R^3 \). Top to bottom: 1D lattice (10\textsuperscript{5}–10\textsuperscript{9} sites), planar Sierpinski gasket (10\textsuperscript{5}–10\textsuperscript{9} sites), and 3D simple cubic lattice (64\textsuperscript{3} sites). Steady states are achieved well below 10\textsuperscript{8} steps.](image-url)
\[-\frac{dp}{dt} = kp^{1+1/\gamma} \quad t \to \infty. \tag{6}\]

This gives an elementary reaction order \(X\):
\[
X = \frac{2 - h}{1 - h} = 1 + \gamma^{-1} \tag{7}
\]
and relates \(X\) to the effective spectral dimension\(^{23-27}\) of the medium. Obviously, for the case of \(h = 0\) \((\gamma = 1)\), the classical result, \(X = 2\), is regained.

The above relation [Eq. (7)] is new. However, for transient reactions it is implicit in Eqs. (4) and (5). The latter have been tested by simulations\(^{21,25,26}\) on both Sierpinski gaskets \((\gamma = 0.68)\) and percolating clusters \((\gamma \approx 2/3)\). We thus expect \(X\) to be 2.46 for the Sierpinski gasket and 2.50 for percolating clusters [except, possibly, 2.53 for 2D percolating clusters\(^{8,27}\)]. A special case is the 1D lattice \((\gamma = 0.5)\), where we expect \(X = 3\) (three).

Experiments were done for the exciton fusion reaction on percolating napthalene clusters.\(^{15}\) For the critical percolation concentration (8%), Fig. 2 of Ref. 12 gives a slope \(X\) of 2.5 \(\pm\) 0.3, in excellent agreement with the theory \((X = 2.5)\) and the measured\(^{21,28}\) \(h = 0.36\) (giving \(X = 2.6\)). Moreover, below percolation, the experiments\(^{16,18}\) give \(h = 0.5\), corresponding to \(X = 3\), while Fig. 2 of Ref. 12 gives \(X = 3.5 \pm 0.5\). [Note, the log (fluorescence) vs log (phosphorescence) curve for the 4% sample is not straight; this is expected well below percolation.]

The above tests on Eq. (7) involved transient kinetics. Does Eq. (7) also hold for steady state kinetics? Extensive Monte Carlo simulations (Fig. 1) show that it does. In the low density limit, the cubic lattice binary reaction (Fig. 1) behaves classically, \(X = 2\), while the Sierpinski gasket behaves "fractally," \(X = 2.45\), and the linear lattice indeed gives \(X = 3\). This is a striking demonstration of the validity of Eq. (7) for steady state reaction rates.\(^{29}\) The high density trends will be discussed elsewhere. We note that two walkers occupying the same site at the instant in time fuse \((A + A \to A)\) and that walkers are placed on the lattice at a constant rate \(R\).

The Cyber 205 supercomputer (Colorado State) was used for the eighth order Sierpinski gasket (100 runs for each \(R\)) and the simple cubic lattice (20 runs for \(R < 5\) and 5–10 runs for larger \(R\)). The uniform pseudorandom number generator RANF was used. The University of Michigan Am- dahl 5860 was used for the 1D lattice simulations (about 5 runs for each \(R\)), using the pseudorandom number generator FUNKIF. Nonlinear regressions were performed to obtain the \(X\) values for Fig. 1.

The classical, diffusion-limited Smoluchowski–Noyes chemical kinetics is based on classical diffusion equations.\(^{30-33}\) An extension to fractal-like media, where the diffusion is anomalous (no diffusion constant) requires a consi
deration of three different dimensions (Euclidean, fractal, and spectral\(^{34}\)). A first step in this direction has now been achieved. Generalizations to pseudounary \((A + B \to B + \text{products})\),
binary \((A + B \to \text{products})\),
and to higher molecularity reactions are in progress, as well as the approach to steady state. Our new approach to low-dimensional chemical kinetics might lead to a new understanding for heterogeneous reactions of technological and biological importance.

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\(^{27}\) Preliminary steady-state simulation results on percolating clusters give \(X = 2.51\), J. S. Newhouse and R. Kopelman (unpublished).

\(^{28}\) M. Noyes, Prog. React. Kin. 6, 128 (1961).

