

siderable information on the potential surfaces involved.

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Fractal chemical kinetics: Simulations and experiments^a

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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,¹ diffusion-limited aggregates² and percolation clusters.³ Diffusion in or on such media is anomalous³⁻⁹ and so are diffusion-limited chemical reactions.¹⁰⁻²² What are the rules for transient and steady state reactions on such media? It has been shown experimentally^{12,13} that an elementary reaction



may have a reaction rate (ρ = density of species A, t = time):

$$-d\rho/dt = k\rho^X \quad X \geq 2, \quad (2)$$

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.^{6-9,23} 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

$$S \propto t^f \quad 0 < f < 1 \quad (t \rightarrow \infty), \quad (3)$$

where $f = 1$ for classical (3D homogeneous) diffusion and $f < 1$ for anomalous diffusion.⁶⁻⁹ It has been shown²⁴ for the fractal exponent f that $f = d_s/2$ for $d_s < 2$. It has also been shown^{14,18,21} that the rate for the simple binary reaction (1) is

$$-d\rho/dt = k_0 t^{-h} \rho^2 \quad 1 > h \geq 0 \quad (t \rightarrow \infty), \quad (4)$$

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.^{21,22,25,26} The integrated rate equation, obtained from Eq. (4), is

$$\rho^{-1} - \rho_0^{-1} = k_0 f^{-1} t^f \quad (\text{if } h = 1 - f), \quad (5)$$

where $\rho_0 \equiv \rho(t=0)$. Hence,^{14,20}

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

A simple substitution of Eq. (5') into Eq. (4) gives ($k \equiv k_0^{1/f} f^{1-1/f}$):

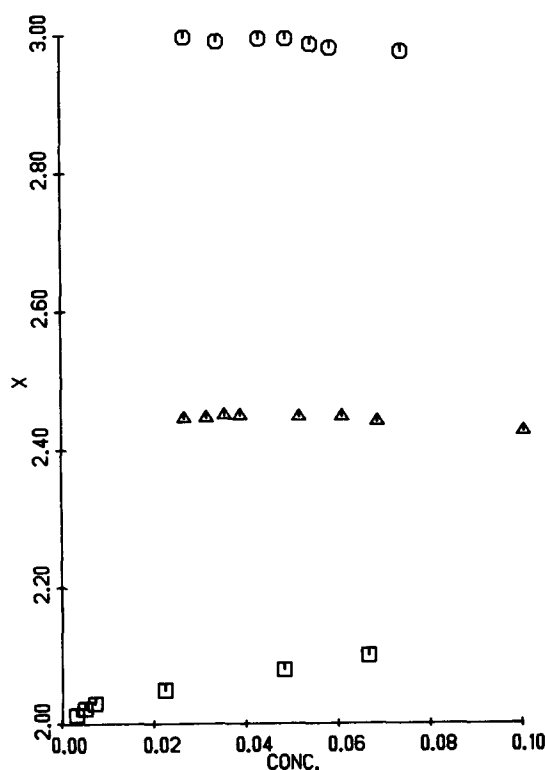


FIG. 1. Effective reaction order X vs the mean steady state walker density, $\text{CONC.} \equiv \langle \rho_{ss} \rangle \propto R^X$. Top to bottom: 1D lattice (10^4 - 10^5 sites), planar Sierpinski gasket ($\sim 10^4$ sites), and 3D simple cubic lattice (64^3 sites). Steady states are achieved well below 10^4 steps.

$$-dp/dt = kp^{1+1/f} \quad t \rightarrow \infty. \quad (6)$$

This gives an elementary reaction order X :

$$X = \frac{2-h}{1-h} = 1 + f^{-1} \quad (7)$$

and relates X to the effective spectral dimension²³⁻²⁷ of the medium. Obviously, for the case of $h = 0$ ($f = 1$), 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 ($f = 0.68$) and percolating clusters ($f \cong 2/3$). 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 ($f = 0.5$), where we expect $X = 3$ (three!).

Experiments were done for the exciton fusion reaction on percolating naphthalene clusters.¹² For the critical percolation concentration (8%), Fig. 2 of Ref. 12 gives a slope X of 2.5 ± 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^{14,18} give $h \cong 0.5$, corresponding to $X \cong 3$, while Fig. 2 of Ref. 12 gives $X \cong 3.5 \pm 0.5$. [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 same instant in time *fuse* ($A + A \rightarrow A$) 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 Amdahl 5860 was used for the 1D lattice simulations (about 5 runs for each R), using the pseudorandom number generator FUNIF. 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^{6,24}). A first step in this direction has now been achieved. Generalizations to

pseudounary ($A + B \rightarrow B + \text{products}$),

binary ($A + B \rightarrow \text{products}$),

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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