LETTER TO THE EDITOR

Time evolution of an irreversible catalytic recombination process

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Abstract. The time evolution of the irreversible catalytic recombination process A + B → inert is studied both analytically and by computer simulation. A rate equation describing this process is derived. For situations where one of the species poisons the catalyst, the minority species, for low coverages, is found to decay exponentially. Computer simulation results confirm this exponential decay for low coverages. Near the poisoning transition, $x_A \simeq x_B$, the average relaxation time is found to diverge as $\zeta \propto (0.5 - x_A)^{-1}$ with $\zeta \simeq 1.3$. Here x_A and x_B are the compositions of A and B in the gas.

The kinetics of the irreversible diffusive recombination process A + B → inert has recently attracted a great deal of experimental and theoretical interest in condensed matter physics and chemical kinetics [1, 2]. The mean-field description of such processes may be written as [3]:

$$dx_A(t)/dt = -k x_A(t) x_B(t) \tag{1}$$

where $x_A(t)$ and $x_B(t)$ are the densities of species A and B at times t and k is the rate constant. A similar rate equation can be written for the evolution of $x_B(t)$. For long times this equation gives

$$x_A(t) \simeq 1/kt \qquad \text{for } x_A(0) = x_B(0) \tag{2a}$$

and

$$x_A(t) \simeq \exp[-k(x_B(0) - x_A(0))t] \qquad \text{for } x_A(0) < x_B(0). \tag{2b}$$

Inclusion of spatial fluctuations in the particle densities, however, gives the asymptotic solutions [1]:

$$x_A(t) \simeq 1/kt^\alpha \qquad \text{for } x_A(0) = x_B(0) \tag{3a}$$

and

$$x_A(t) \simeq \exp[-c(x_B(0)^{1/2} - x_A(0)^{1/2})t^\alpha] \qquad \text{for } x_A(0) < x_B(0) \tag{3b}$$

with $\alpha = d/4$.

To our knowledge very little similar published literature exists for the corresponding catalytic irreversible recombination process A + B → inert, where the species react with each other only after getting adsorbed onto a catalytic surface. In contrast to the diffusive recombination process where the reactants A and B are not replenished during the reaction, in this case both the reactants are constantly being replenished from the

gas. We consider a situation where the supply of A and B is unlimited and their diffusion coefficients are infinite, so that x_A and x_B are time independent. For situations where the desorption of A and B, after their adsorption, may be neglected and the reaction product AB instantly leaves the surface, the catalyst eventually becomes poisoned by one or other of the reactants except when $x_A = x_B$ [4]. For $x_B > x_A$ the number of minority adsorbed species per lattice site, θ_A, decays with time. The closer one is to the poisoning transition $x_A = x_B$, the slower is the decay of θ_A.

In analogy with the surface reaction model for the catalytic oxidation of carbon monoxide [4, 5] we assume an infinite reservoir of reactants A and B in the gas of compositions x_A and x_B; $x_A + x_B = 1$. The desorption of A and B from the catalytic surface is neglected. The reaction product AB, which is formed only when A and B occupy nearest-neighbour sites, instantly leaves the catalytic surface. In this case the adsorption of A atoms next to adsorbed A atoms leads to the enhancement of θ_A while that of B atoms will consume A atoms already adsorbed. The probability of occurrence of both these processes is proportional to $\bar{b}(\theta_A)$, the average number of vacancies neighbouring the adsorbed A atoms per unit active site of the catalyst. New islands of A can also become nucleated in regions away from adsorbed A and B atoms. If we ignore the contributions of such islands to $\theta_A(t)$ then in the mean-field approximation we may write

$$\mathrm{d}\theta_A(t)/\mathrm{d}t = -k(x_B - x_A)\bar{b}(\theta_A) \qquad \text{for } x_B > x_A \qquad (4)$$

where k is a rate constant which includes both the reaction and adsorption rates.

The average cluster size $\bar{s}(\theta_A)$ per unit active site and $\bar{b}(\theta_A)$ are both expected to increase with θ_A. If we assume that†

$$\bar{b}_A(\theta) \propto \theta_A^\delta \qquad (5)$$

then (4) gives

$$\theta_A(t) \propto \exp\left[-(x_B - x_A)t^\alpha\right] \qquad \text{for } \delta = 1 \qquad (6a)$$

and

$$\theta_A(t) \propto 1/t^{1/(\delta-1)} \qquad \text{for } \delta \neq 1. \qquad (6b)$$

In order to test these ideas we have simulated the model system for the irreversible catalytic recombination process described above. We started with an empty lattice of 40×40 sites, using periodic boundary conditions. Figure 1 shows the results of $\bar{b}(\theta_A)$ as a function of θ_A. We can distinguish two different regimes, with the transition between them taking place for coverage θ_A lying between 0.01 and 0.02. The value of

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† For very small values of θ_A one expects clusters to be well separated, so that $\bar{b}(\theta_A) = \Sigma_s\, n_s b_s / \Sigma_s\, n_s$, where n_s is the number of A clusters of size s with b_s as its boundary. At low coverages the clusters are small in size and their perimeter is proportional to their size, while at higher coverages less than the percolation threshold we expect to get ramified clusters. In either case $b_s \propto s$, so that

$$\bar{s} = \Sigma sn_s / \Sigma ns = \theta_A$$

$$\bar{b}(\theta_A) = \Sigma b_s n_s / \Sigma n_s \simeq \Sigma sn_s = \bar{s} = \theta_A$$

and in general we may write
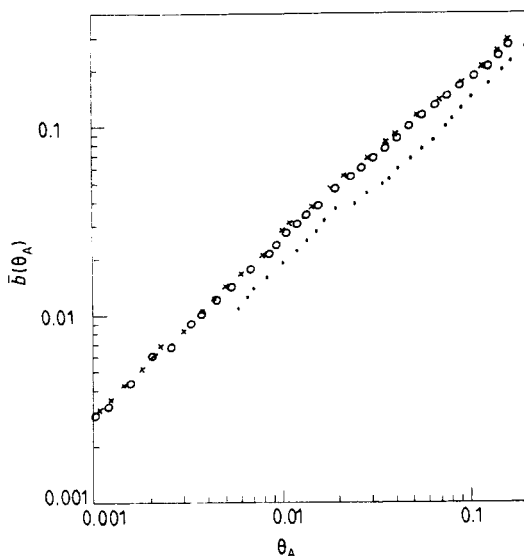
$$\bar{b}(\theta_A) \simeq \theta_A^\delta.$$

Figure 1. Average number of vacancies $\bar{b}(\theta_A)$ neighbouring the adsorbed A atoms plotted against the coverage θ_A of the minority species on a log–log scale for concentrations: 0.501 (●); 0.503 (○); 0.505 (×).

δ as given by the slope of the curves changes from 1.00 ± 0.05 for low coverages (longer times) to a value less than unity for higher coverages (intermediate times). In order to see the effect of still higher coverages of the minority species (θ_A) on δ, we started the simulation with a lattice that is initially 75% covered with the A type of atoms. For low coverages we get agreement with the results obtained with an empty lattice, while for higher coverages, $\bar{b}(\theta_A)$ goes to a maximum and decays again with further increase of coverage. This suggests that equation ($6a$) corresponding to an exponential decay is valid only in the asymptotic limit of low coverages.

The simulation results for $\theta_A(t)$ as a function of time (figure 2) seem to confirm this contention. We find that indeed the coverage $\theta_A(t)$ decays exponentially for low coverages (less than 0.1). For very low coverages, however, we get a certain deviation from this exponential behaviour. A plausible explanation is linked to the statistics of our results. For longer times (low coverages) one gets a scatter in the results due to the fact that the closer one is to the poisoning transition the greater are the fluctuations in θ_A. Moreover, the time after which the catalyst gets poisoned also fluctuates over a wide range. Though the results shown are averaged over 400 different runs, the averaging for longer times (low coverages) is over smaller and smaller runs due to this factor. It is therefore possible that the deviation from an exponential behaviour is only a statistical anomaly, and our results are consistent with an exponential behaviour, as predicted by the analytical treatment for $\delta = 1$.

The relaxation time given by the inverse of the slope of the straight portions in figure 2 becomes larger and larger as one approaches the poisoning transition. The relaxation times are plotted in figure 3 as a function of $(0.5 - x_A)$. Close enough to the poisoning transition, $x_B = x_A = 0.5$, one gets a straight line with a slope $\gamma \simeq 1.3$.

Preliminary calculations on the irreversible catalytic reaction of carbon monoxide and oxygen to form carbon dioxide suggest a value of $\delta = 1$ and an exponential decay for the coverage (adsorbed oxygen atoms) for both intermediate and long times [6].
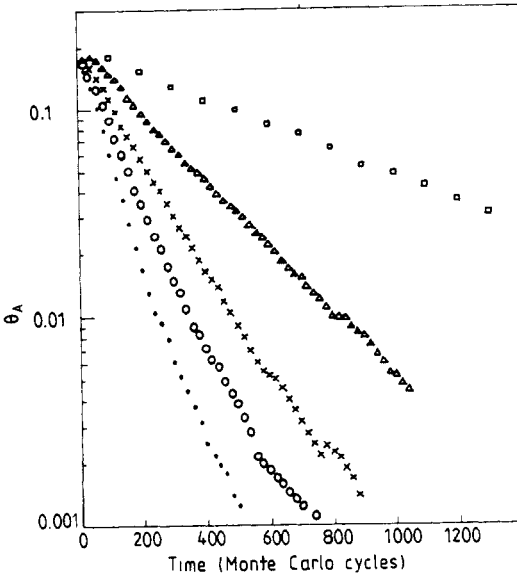
Figure 2. Coverage θ_A of the minority species plotted against time on a semilog scale for concentrations: 0.501 ($\square$); 0.502 ($\triangle$); 0.503 ($\times$); 0.504 ($\bigcirc$); 0.505 ($\bullet$).
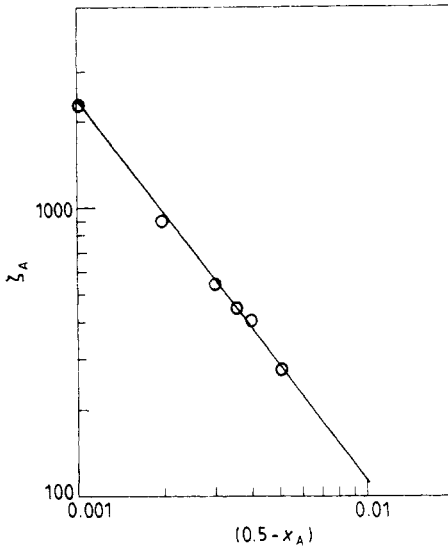

Figure 3. The relaxation time ζ_A plotted against the difference in composition $(0.5 - x_A)$. The line is drawn as an aid to the eye.

References

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