

## Stochastic model for complex surface-reaction systems with application to $\text{NH}_3$ formation

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(Received 5 March 1993)

A stochastic model is introduced that is appropriate to describe surface-reaction systems. These reaction systems are well suited for the description via master equations using their Markovian behavior. In this representation an infinite chain of master equations for the distribution functions of the state of the surface, of pairs of surface sites, etc., arises. This hierarchy is truncated by a superposition approximation. The resulting lattice equations are solved in a small region which contains all of the structure-sensitive aspects and can be connected to continuous functions which represent the behavior of the system for large distances from a reference point. In the present paper, we focus our interest on the development of the formalism and its use when applied to the formation of  $\text{NH}_3$ . The results obtained (phase-transition points and densities of particles on the surface) are in agreement with Monte Carlo and cellular-automata simulations. The stochastic model can easily be extended to other reaction systems and is therefore an elegant alternative to the description via Monte Carlo and cellular-automata simulations.

PACS number(s): 05.40.+j, 05.50.+q, 02.50.-r

### I. INTRODUCTION

Catalytic reactions on solid surfaces are of great complexity and they are thus inherently very difficult to deal with. The detailed understanding of such reactions is very important in applied research, but rarely has such a detailed understanding been achieved neither from experiment nor from theory. Theoretically there are three possible approaches, kinetic equations of the mean-field type, computer simulations [Monte Carlo (MC) and cellular automata (CA)], or stochastic models (master equations). Kinetic equations are useful as a fitting procedure although their basis—the homogeneous system—is in general nonexistent. Thus they cannot deal with segregation and island formation, which are frequently observed [1]. Computer simulations keep the fluctuations and correlations and are thus able to deal with segregation effects and the like, but so far the reaction systems are very simplified ones containing only a few aspects of a real system. The use of computer simulation for the study of surface-reaction systems is limited because of the large amount of computer time needed. MC simulations especially need so much computer time that complicated aspects (e.g., the dependence of the results on the distribution of surface defects) cannot be studied in practice. For this reason we have developed CA models that run very fast on parallel computers and enable us to study more complex aspects of reaction systems. Examples of CA models that have been studied in the past are  $\text{NH}_3$  forma-

tion [2], the question of the universality class [3], and diffusion as well as diffusion-reaction of the  $A + B_2$  surface-reaction system [4]. But CA models are limited to systems that are suited for the description by a purely parallel ansatz.

Master equations present a very powerful and general approach because they also maintain correlations, fluctuations, and structural information. Their use for complex reaction systems which take place on a lattice is only limited by the fact that they can, up to now, only be solved for very simple systems in one dimension analytically [5]. But it is possible to introduce sensible approximations and/or solve the equations numerically. For example, certain aspects of the problem can be solved analytically instead by a purely numerical approach and one does not attempt to include structural effects and fluctuations at large distances where by necessity these have to die out. Many different approaches have been developed to handle such systems. Some important references are cited in Ref. [6].

In this paper we introduce a stochastic model for surface-reaction systems which represents an elegant alternative to the description via MC and CA simulations. As an application we focus our interest on the formation of  $\text{NH}_3$ , which is described below [Eqs. (1)–(5)]. It is expected that these stochastic systems are well suited for the description via master equations using the Markovian behavior of the systems. In such a representation an infinite chain of master equations for the distribution

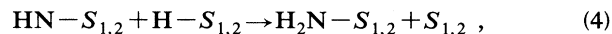
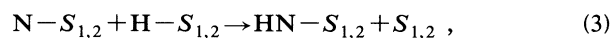
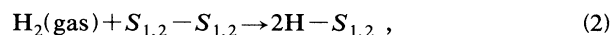
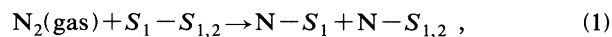
functions of the state of the surface and of pairs of surface sites (and so on) will arise. The chain of equations cannot be solved analytically. To handle this problem practically this hierarchy must be truncated at a certain level. The resulting equations can be solved exactly in a small region and can be connected to a mean-field solution for large distances from a reference point. This procedure is well suited for the description of surface-reaction systems which includes the steps of adsorption, diffusion, reaction, and desorption. The numerical part needs only a very small amount of computer time compared to MC or CA simulations. In spite of very simple theoretical descriptions (for example, mean-field descriptions for certain aspects) structural aspects of the systems are explicitly taken into account. This leads to results that are in agreement with computer simulations. But the stochastic model avoids the main difficulty of computer simulations: the tremendous amount of computer time needed to obtain good statistics for the results. Therefore more complex systems can be studied in detail, which may eventually lead to a better understanding of such systems. In the theoretical sections below we shall deal with a disordered surface. This additional complication can be handled with the stochastic approach. This is also a very important case in catalytic reactions.

The equations are written specifically for the  $\text{NH}_3$  formation as a fully general approach would be unwieldy. The modification of the approach to other reactions cannot be considered as trivial but can be done following the outline below. Another application to a very complex reaction system ( $\text{CO} + \text{O}_2$  on a Pt-Sn disordered catalyst) will demonstrate this as well as the generality of the stochastic ansatz [7].

The knowledge of the details of catalytic reaction systems is in general of great industrial importance. Much effort in particular has been undertaken to understand the reaction mechanism of the  $\text{NH}_3$  synthesis. But even today this system is not well understood because it turns out to be very complex. With the help of modern surface spectroscopy methods some aspects of the reaction mechanism [8] and some details of the role of structural and energetic promoters on the surface have been clarified but no consensus has been reached on several important points. The  $\text{NH}_3$  synthesis is industrially performed with a promoted iron catalyst, where the promoters are structural ones such as  $\text{Al}_2\text{O}_3$  and electronic ones such as  $\text{K}_2\text{O}$ . In the laboratory, single crystals of iron, tungsten, or rhenium are used.  $\text{H}_2$  adsorbs dissociatively with a large sticking coefficient and  $\text{N}_2$  adsorbs molecularly with an activation barrier towards dissociation into atoms which together lead to a low sticking coefficient of about  $10^{-7}$ . The dissociative adsorption is the rate-limiting step. The sticking coefficient is defined as the probability that a molecule impinging on the surface is adsorbed (dissociatively). The reaction occurs between adsorbed atoms via the steps  $\text{N} + \text{H} \rightarrow \text{NH}$ ,  $\text{NH} + \text{H} \rightarrow \text{NH}_2$ , and, finally,  $\text{NH}_2 + \text{H} \rightarrow \text{NH}_3$ , which desorbs after formation. Computer simulations are another tool which may be helpful for understanding certain aspects of the behavior of this system. Complex kinetic and thermodynamic cal-

culations have been introduced by Stoltze and Norskov [9] who take many aspects of the reaction system into account. Their results are in very good agreement with experimental observations of the reaction rate. Due to the use of many experimental data their model becomes involved and one cannot understand the evolution of the reaction system in detail.

We have introduced a CA model for  $\text{NH}_3$  formation [2]. This model accounts only for a few aspects of the reaction system. In our simulation the surface is represented as a two-dimensional square lattice with periodic boundary conditions. A gas phase containing  $\text{N}_2$  and  $\text{H}_2$  with the mole fraction of  $y_{\text{N}}$  and  $y_{\text{H}} = 1 - y_{\text{N}}$ , respectively, sits above this surface. Because the adsorption of  $\text{H}_2$  is dissociative a  $\text{H}_2$  molecule requires two adjacent vacant sites. The adsorption rule for the  $\text{N}_2$  molecule is more difficult to describe because experiments show that the sticking coefficient of  $\text{N}_2$  is unusually small ( $10^{-7}$ ). The adsorption probability can be increased by high-energy impact of  $\text{N}_2$  on the surface. This process is interpreted as tunneling through the barrier to dissociation [10]. Another possibility to increase the adsorption probability is via electronic promoters ( $\text{K}_2\text{O}$ ). It is believed that this promoter, which is enriched on the surface, leads to a larger binding energy of molecular  $\text{N}_2$  via an increased metal  $\pi$ -electron backbonding. Connected with this is a lowering of the activation energy for dissociation [11]. Because of the presence of promoters we introduce two different adsorption sites: activated ones,  $S_1$ , and normal ones,  $S_2$ . We suppose that the dissociative adsorption of  $\text{N}_2$  occurs on a pair of neighboring vacant sites from which at least one must be activated ( $S_1$ - $S_{1,2}$ ), where  $S_{1,2}$  means a surface site of type 1 (activated) or 2 (nonactivated). It is unnecessary to require two neighboring activated sites for the dissociative adsorption of  $\text{N}_2$ . The effect of the promoter is not a strictly localized one but also influences the neighborhood. At the typical concentrations of  $\text{K}^+$  it is rather unlikely that two neighbor sites are both activated. Thus our rules take into account the fact that an activated site also influences the energetic behavior of the neighboring sites. The dissociative adsorption of  $\text{H}_2$  can take place on every pair of free sites  $S_1$ - $S_1$ ,  $S_1$ - $S_2$  or  $S_2$ - $S_2$ . The concentration of  $S_1$  is a measure for the concentration of  $\text{K}^+$  on the surface. If a N atom is a nearest neighbor of a H atom reaction occurs to  $\text{NH}$ - $S_{1,2}$ . Via further reaction steps the product molecule  $\text{NH}_3$  is formed which desorbs immediately after formation. We neglect recombination reactions. Therefore the basic steps are



We neglected in our model the back reactions to simplify

the already quite complicated process. In some of the steps this does not correspond to the reality, with the exception of the last step, because  $\text{NH}_3$  is removed from the surface and the reactor. We do not believe that the inclusion of the back reactions will alter significantly the conclusions of the present very simplified reaction model except via a reduced reaction rate. The surface coverages should remain essentially unchanged and they are the prominent information from our model. Further on the removal of  $\text{NH}_3$  introduces a "drag" on the reaction process in the direction of smaller importance of the back reactions. As a result of our model we found for the case where all sites are activated a first-order kinetic phase transition for the coverages as a function of  $y_N$ . For  $y_N < y_1 = 0.262$  the surface is nearly completely covered by H and nearly no reaction takes place. With decreasing  $y_N$ , the coverage of H ( $\Theta_H$ ) increases to unity. For the value  $y_N = 0$  itself only  $\text{H}_2$  molecules adsorb and no reaction event occurs. Therefore  $\Theta_H = 0.88$ , which is the maximum coverage for the adsorption of dimers. For the case that not all sites are activated a change in the character of the phase transition from first to second order is observed.

The paper is structured as follows: In Sec. II we introduce the stochastic model. The representation of the state of the lattice sites (activated or unactivated) and their occupation with particles are introduced. The distribution functions are defined in Sec. III. The resulting lattice equations which represent the temporal evolution of the distribution functions are represented in Sec. IV. The superposition approximation which is used is discussed in Sec. V. Section VI deals with the numerical procedure which we use to solve the lattice equations. The results for the formation of  $\text{NH}_3$  are presented in Sec. VII. The discussion of the results and the comparison to an earlier presented CA model for the  $\text{NH}_3$  formation [2] takes place in Sec. VIII.

## II. STOCHASTIC MODEL

### A. Surface

In our simulation we use a square lattice (but this is not a necessary condition; different lattices pose no problem).

$$\left. \begin{array}{l} P(0,0) = (1-S)^2 + \Gamma \geq 0 \\ P(0,1) = S(1-S) - \Gamma \geq 0 \\ P(1,1) = S^2 + \Gamma \geq 0 \end{array} \right\} \Rightarrow \begin{cases} -S^2 < \Gamma < S(1-S) & \text{for } S \leq 0.5 \\ -(1-S)^2 < \Gamma < S(1-S) & \text{for } S > 0.5 \end{cases} \quad (12)$$

One obtains as limiting cases:

$\Gamma = S(1-S) \Rightarrow P(0,1) \equiv 0 \Rightarrow$  no  $a$ - $u$  pairs exist at the distance  $|l-m|$ .

For  $S \leq 0.5$ ,  $\Gamma = -S^2 \Rightarrow P(1,1) \equiv 0 \Rightarrow$  no  $a$ - $a$  pairs exist at the distance  $|l-m|$ .

For  $S > 0.5$ ,  $\Gamma = -(1-S)^2 \Rightarrow P(0,0) \equiv 0 \Rightarrow$  no  $u$ - $u$  pairs exist at the distance  $|l-m|$ .

Each lattice site is given a lattice vector  $l$ . The state of the site  $l$  (activated or unactivated) is represented by the lattice variable  $\sigma_l$  with

$$\sigma_l = \begin{cases} 0 & \text{if the site is unactivated (u)} \\ 1 & \text{if the site is activated (a)} \end{cases} \quad (6)$$

We define  $S = \langle \sigma_l \rangle$  as the mean value of the activity of the catalyst and this is independent of  $l$ . Next we introduce the correlation of the activated and unactivated sites:

$$G(l-m) = \langle \sigma_l \sigma_m \rangle. \quad (7)$$

In the asymptotic limit where the cells  $l$  and  $m$  are far away from each other we obtain

$$\lim_{|l-m| \rightarrow \infty} G(l-m) = S^2, \quad (8)$$

which expresses the fact that the correlation between the sites vanishes. For finite distances we define  $G$  as

$$G(l-m) = S^2 + \Gamma(l-m). \quad (9)$$

For  $\Gamma = 0$  we get an uncorrelated distribution of activated and unactivated sites. With the help of these definitions we are able to express the disorder of the surface states by assigning each cell a probability

$$P(\sigma_l) = (1-S) + \sigma_l(2S-1) \quad (10)$$

and for a pair of cells

$$\begin{aligned} P(\sigma_l, \sigma_m) = & [(1-S)^2 + \Gamma] \\ & + (\sigma_l + \sigma_m)[(2S-1)(1-S) - 2\Gamma] \\ & + \sigma_l \sigma_m [(2S-1)^2 + 4\Gamma]. \end{aligned} \quad (11)$$

All probabilities must be positive, which means:

$\Gamma$  as a function of the distance must fulfill these conditions.

### B. Particles

We introduce a variable for the particles  $\gamma \in \{0, \text{H}, \text{N}, \text{A}, \text{B}\}$ , where 0 represents a vacant site,  $A$

represents a NH particle and  $B$  a  $\text{NH}_2$  particle. The state of a lattice point  $\chi_l$  consists of the state of the catalyst (activated or unactivated) and its coverage with a particle. This leads to the following possible states:

$$\chi_l = \{\gamma_l \sigma_l\} \equiv 0u, 0a, Hu, Ha, \dots, Bu, Ba. \quad (13)$$

The H and N particles are created on the surface by adsorption out of the gas phase with the rates

$$p_{\text{H}_2} = y_{\text{H}} \quad \text{and} \quad p_{\text{H}} = 2p_{\text{H}_2} = 2y_{\text{H}} \quad (14)$$

for the H particles and

$$p_{\text{N}_2} = 1 - y_{\text{H}} \quad \text{and} \quad p_{\text{N}} = 2(1 - y_{\text{H}}) \quad (15)$$

for the N particles.  $y_{\text{H}}$  and  $y_{\text{N}}$  are the mole fraction of  $\text{H}_2$  and  $\text{N}_2$  in the gas phase with  $y_{\text{H}} + y_{\text{N}} = 1$ . By these adsorption steps pairs of HH and NN particles are created because of the dissociative character of the adsorption. For the adsorption of  $\text{N}_2$  at least one of the lattice sites must be activated:  $\sigma_l + \sigma_m > 0$ . This condition appears implicitly very often in the following but we do not write it explicitly.

At normal temperatures H atoms are very mobile on metal surfaces. We take this into account by the possibility of diffusion steps for the H atoms. A H atom jumps with rate  $D$  onto nearest-neighbor sites on the lattice. If this site is occupied by N reaction occurs and an A particle (NH particle) is formed. The same holds if the site is occupied by A or B ( $\text{NH}_2$ ), where the products B or  $\text{NH}_3 \equiv 0$  are formed, respectively.  $\text{NH}_3$  desorbs immediately from the surface and an empty site is formed. This type of reaction system is called a *diffusion-limited* reaction system. It is important to note that all the reaction steps discussed above (with the exception of the  $\text{N}_2$  adsorption) are independent of  $\sigma_l$  and  $\sigma_m$ . In the following we normalize the adsorption and the diffusion rate to the coordination number  $z$  of the lattice ( $z=4$  for the square lattice):  $p_{\text{N,H}} \rightarrow p_{\text{N,H}}/z$  and  $D \rightarrow D/z$ .

### III. DISTRIBUTION FUNCTIONS

Next we want to define the distribution function  $\rho^{(k)}$  of order  $k$  for the state of the surface. For  $k=1$  we get

$$\rho^{(1)} = \rho^{(1)}(\chi_l) = \rho^{(1)}(\gamma_l \sigma_l) = C_{\chi} \equiv C_{\gamma}^{\sigma}(t). \quad (16)$$

$C_0^u, C_0^a, \dots, C_B^a$  are the lattice densities which are independent of  $l$  because of the translatory invariance of the lattice. One of the densities depends on the others because of the sum rule

$$\sum_{\chi_l} \rho^{(1)} \equiv 1. \quad (17)$$

The distribution functions of second order ( $k=2$ )  $\rho^{(2)} = \rho^{(2)}(\chi_l \chi_m)$  depends on the distance ( $l-m$ ). As an asymptotic case one obtains

$$\lim_{|l-m| \rightarrow \infty} \rho^{(2)} = \rho^{(1)}(\chi_l) \rho^{(1)}(\chi_m). \quad (18)$$

We define the correlation functions as follows:

$$F_{\chi_l \chi_m}(l-m) = \frac{\rho^{(2)}(\chi_l \chi_m)}{\rho^{(1)}(\chi_l) \rho^{(1)}(\chi_m)}. \quad (19)$$

Because of the sum rule

$$\sum_{\chi_m} \rho^{(2)}(\chi_l \chi_m) = \rho^{(1)}(\chi_l) \quad (20)$$

10 of the total 55 correlation functions are dependent variables. The correlation functions are normalized via the 10 conditions

$$\sum_{\chi'} C_{\chi'} F_{\chi \chi'}(l-m) = 1. \quad (21)$$

Distribution functions of third order  $\rho^{(3)}$  ( $k=3$ ) will be approximated by the superposition approximation of Kirkwood [12]:

$$\begin{aligned} \rho^{(3)}(\chi_l \chi_m \chi_n) &= C_{\chi_l} C_{\chi_m} C_{\chi_n} F_{\chi_l \chi_m}(l-m) \\ &\quad \times F_{\chi_m \chi_n}(m-n) F_{\chi_n \chi_l}(n-l). \end{aligned} \quad (22)$$

Higher-order distribution functions ( $k > 3$ ) will be neglected in our model because they can hardly be handled and they should not be as important for the present and similar reactions as the lower-order distribution functions.

### IV. EXACT LATTICE EQUATIONS

With the help of the definitions made above we are able to write the equations for the temporal evolution of the distribution functions.

#### A. One-point probabilities

The general form of the equation of motion for the one-point probabilities is

$$\frac{\partial}{\partial t} \rho^{(1)}(\chi_l) = \left\{ \frac{\partial}{\partial t} X \right\} \quad (23)$$

with  $X \in \{0, \text{H}, \text{N}, \text{A}, \text{B}\}$ . The brackets on the right-hand side represent the state at site  $l$ . In the following we use the definition

$$\alpha_{l,m} = \begin{cases} 1 & \text{if } l \text{ and } m \text{ are nearest neighbors} \\ 0 & \text{otherwise} \end{cases}. \quad (24)$$

The temporal evolution of the B density is given by

$$\frac{\partial}{\partial t} C_B^{\sigma} = D \left[ C_A^{\sigma} \sum_{\sigma'} C_H^{\sigma'} F_{A\sigma H\sigma'}(1) - C_B^{\sigma} \sum_{\sigma'} C_H^{\sigma'} F_{B\sigma H\sigma'}(1) \right]. \quad (25)$$

$F_{\sigma\sigma'}(1)$  is the correlation function for nearest neighbors. The other densities are given by the following equations of motion. For the A density:

$$\frac{\partial}{\partial t} C_A^\sigma = D \left[ C_N^\sigma \sum_{\sigma'} C_H^{\sigma'} F_{N\sigma H\sigma'}(1) - C_A^\sigma \sum_{\sigma'} C_H^{\sigma'} F_{A\sigma H\sigma'}(1) \right]. \quad (26)$$

For the N density:

$$\frac{\partial}{\partial t} C_N^\sigma = p_N C_0^\sigma \sum_{\sigma'} C_0^{\sigma'} F_{0\sigma 0\sigma'}(1) - DC_N^\sigma \sum_{\sigma'} C_H^{\sigma'} F_{N\sigma H\sigma'}(1). \quad (27)$$

For the H density:

$$\begin{aligned} \frac{\partial}{\partial t} C_H^\sigma &= p_H C_0^\sigma \sum_{\sigma'} C_0^{\sigma'} F_{0\sigma 0\sigma'}(1) + DC_0^\sigma \sum_{\sigma'} C_H^{\sigma'} F_{0\sigma H\sigma'}(1) \\ &- DC_H^\sigma \left[ \sum_{\sigma'} C_0^{\sigma'} F_{H\sigma 0\sigma'}(1) + \sum_{\sigma'} C_N^{\sigma'} F_{H\sigma N\sigma'}(1) + \sum_{\sigma'} C_A^{\sigma'} F_{H\sigma A\sigma'}(1) + \sum_{\sigma'} C_B^{\sigma'} F_{H\sigma B\sigma'}(1) \right]. \end{aligned} \quad (28)$$

For the 0 density:

$$\begin{aligned} \frac{\partial}{\partial t} C_0^\sigma &= -p_H C_0^\sigma \sum_{\sigma'} C_0^{\sigma'} F_{0\sigma 0\sigma'}(1) - p_N C_0^\sigma \sum_{\sigma'} C_H^{\sigma'} F_{0\sigma H\sigma'}(1) \\ &- DC_0^\sigma \left[ \sum_{\sigma'} C_0^{\sigma'} F_{H\sigma 0\sigma'}(1) + \sum_{\sigma'} C_N^{\sigma'} F_{H\sigma N\sigma'}(1) + \sum_{\sigma'} C_A^{\sigma'} F_{H\sigma A\sigma'}(1) + \sum_{\sigma'} C_B^{\sigma'} F_{H\sigma B\sigma'}(1) \right] \\ &+ DC_B^\sigma \sum_{\sigma'} C_H^{\sigma'} F_{B\sigma H\sigma'}(1) - DC_0^\sigma \sum_{\sigma'} C_H^{\sigma'} F_{0\sigma H\sigma'}(1). \end{aligned} \quad (29)$$

### B. Two-point probabilities

The general form of the two-point probabilities reads in the diagrammatic description:

$$\rho^{(2)}(\chi_l \chi_m) = \begin{bmatrix} \mathbf{x} & - & \mathbf{y} \\ l & & \mathbf{m} \end{bmatrix}, \quad (30)$$

with  $X, Y \in \{0, H, N, A, B\}$ . The right-hand side denotes the two-point probabilities with species  $X$  at site  $l$  and  $Y$  at site  $\mathbf{m}$ . The hyphen here and below denotes that there is a correlation between  $X$  and  $Y$ . Differentiation leads to

$$\begin{aligned} \frac{\partial}{\partial t} \rho^{(2)}(\chi_l \chi_m) &= \left\{ \frac{\partial}{\partial t} X \right\} - \{Y\} + \{X\} - \left\{ \frac{\partial}{\partial t} Y \right\} \\ &+ \frac{\alpha_{l,m}}{z} \{XY\}. \end{aligned} \quad (31)$$

The first term on the right-hand side describes the change of the state of point  $l$  which does not depend on  $\mathbf{m}$ . The second term expresses the analogous quantity for point  $\mathbf{m}$ . If  $l$  and  $\mathbf{m}$  are nearest neighbors, the change of the states of  $l$  and  $\mathbf{m}$  depend on each other. This fact is taken into account by the third term. The temporal evolution of a state of a cell  $\{\partial X/\partial t\}$  are given in the preceding section.

$\{XY\}$  takes the following values:

$$\{XY\} \equiv 0 \text{ for } X, Y = A, B, \quad (32)$$

$$\{NY\} \equiv 0 \text{ for } Y = A, B, \quad (33)$$

$$\{NN\} = p_N(00) \text{ for } \sigma + \sigma' > 0, \quad (34)$$

$$\begin{aligned} \{HH\} &= p_H(00), \quad \{HN\} = -D(HN), \\ \{HA\} &= -D(HA), \end{aligned} \quad (35)$$

$$\begin{aligned} \{HB\} &= -D(HB), \\ \{00\} &= D(HB + BH) - p_H(00) - p_N(00), \end{aligned} \quad (36)$$

$$\{0H\} = D(H0) - D(0H), \quad \{0N\} \equiv 0, \quad (37)$$

$$\{0A\} = D(HN), \quad \{0B\} = D(HA). \quad (38)$$

The three-point probabilities will be solved by using the Kirkwood approximation:

$$\begin{aligned} \frac{1}{z} \sum_{n, \sigma_n} \alpha_{n,l} \rho^{(3)}(\chi_l \chi_n \chi_m) &= C_{\chi_l} C_{\chi_m} F_{\chi_l \chi_m}(l - \mathbf{m}) \\ &\times \sum_{\sigma_n} C_{\chi_n} \hat{F}_{\chi_n \chi_m}(l - \mathbf{m}) F_{\chi_l \chi_n}(1), \end{aligned} \quad (39)$$

with

$$\hat{F}_{\chi\chi'}(l) = \frac{1}{z} \sum_n \alpha_{n,l} F_{\chi\chi'}(\mathbf{n}), \quad (40)$$

which is the mean value over the lattice. Here we use the additional definition

$$F_{\chi\chi'}(0) = 0. \quad (41)$$

$F_{\chi\chi'}(l)$  can be calculated via the two-point probabilities using the ansatz:

$$\rho^{(2)}(\chi_l \chi_m) = C_{\chi_l} C_{\chi_m} F_{\chi_l \chi_m}(l - \mathbf{m}). \quad (42)$$

For example, let us calculate  $F_{A\sigma B\sigma'}(l)$ :

$$\begin{aligned}
\frac{\partial}{\partial t} F_{A\sigma B\sigma'}(l) = & D \frac{C_A^\sigma}{C_A^\sigma} F_{N\sigma B\sigma'}(l) \sum_{\sigma^*} C_H^{\sigma^*} F_{H\sigma^* N\sigma}(1) \hat{F}_{H\sigma^* B\sigma'}(l) \\
& + D \frac{C_A^{\sigma'}}{C_B^{\sigma'}} F_{A\sigma A\sigma'}(l) \sum_{\sigma^*} C_H^{\sigma^*} F_{H\sigma^* A\sigma'}(1) \hat{F}_{H\sigma^* A\sigma'}(l) - F_{A\sigma B\sigma'}(l) \\
& \times \left[ D \sum_{\sigma^*} C_H^{\sigma^*} F_{H\sigma^* A\sigma'}(1) \hat{F}_{H\sigma^* B\sigma'}(l) \right. \\
& \left. + D \sum_{\sigma^*} C_H^{\sigma^*} F_{H\sigma^* B\sigma'}(1) \hat{F}_{H\sigma^* A\sigma'}(l) + \frac{\partial}{\partial t} \frac{C_A^\sigma}{C_A^\sigma} + \frac{\partial}{\partial t} \frac{C_B^{\sigma'}}{C_B^{\sigma'}} \right]. \quad (43)
\end{aligned}$$

The first term represents the creation of  $A$  from  $N$ , the second the creation of  $B$  from  $A$ , and the third and fourth the annihilation of  $A$  and  $B$ , respectively. The last two terms arise during the transition from  $\rho^{(2)}$  to  $F$ .

### V. SUPERPOSITION APPROXIMATION

The use of the superposition approximation leads to a problem that is typical for lattice systems: the choice of the dependent correlation functions. From the normalization equation (21) the dependent variables can be written as

$$F_{\chi\chi^*}(l) = \left[ 1 - \sum_{\chi' (\neq \chi^*)} C_{\chi'} F_{\chi\chi'}(l) \right] / C_{\chi^*}. \quad (44)$$

Many possibilities exist for choosing some correlation functions as dependent ones because the superposition approximation is a multiplicative approximation which contradicts the sum rule

$$\sum_{\chi_m} \rho^{(3)}(\chi_l \chi_n \chi_m) = \rho^{(2)}(\chi_l \chi_n). \quad (45)$$

Therefore any chosen definition leads to a different form of the resulting equations. Some of these forms may cause numerical difficulties. Therefore the question arises how such cases can be avoided. To this end we write the condition of Eq. (2) in the dynamical form

$$\frac{\partial}{\partial t} \rho^{(1)}(\chi_l) = \sum_{\chi_m} \frac{\partial}{\partial t} \rho^{(2)}(\chi_l \chi_m). \quad (46)$$

If we choose all  $F_{\chi\chi'}(l)$  as independent the use of the superposition approximation leads to an error

$$O_{SA} \left\{ \sum_Z \left( \left[ \begin{array}{c} Y \\ \boxed{X} \\ 1 \end{array} \right] \text{---} Z \right) \right\} = (XY) \sum_Z C_Z F_{XZ}(l-m) \hat{F}_{XZ}(l-m), \quad (51)$$

where

$$\sum_Z C_Z F_{XZ}(l-m) \hat{F}_{XZ}(l-m) / (1 - \alpha_{l,m}/z) = 1/W(X, Y) \neq 1. \quad (52)$$

To avoid this error we use in the numerical procedure the superposition approximation with the correction factor  $W(X, Y)$ :

$$\frac{\partial}{\partial t} \rho^{(1)}(\chi_l) \neq \sum_{\chi_m} O_{SA} \left[ \frac{\partial}{\partial t} \rho^{(2)}(\chi_l \chi_m) \right], \quad (47)$$

where  $O_{SA}$  indicates the superposition approximation. The terms which lead to this error are of the form

$$\left[ \begin{array}{c} Y \\ \boxed{X} \\ 1 \end{array} \right] \text{---} Z \quad m \quad (48)$$

We use the above diagrammatic notation to avoid very cumbersome and lengthy mathematical expressions, which tend to veil the essentials. A square in the diagram means a summation over nearest neighbors. In the middle of the square the central site  $l$  with the particle occupying it is shown. The summation runs over sites  $k$  which are nearest neighbors of site  $l$  and which are occupied with a particle of the type specified by the symbol in the upper right corner of the square. At the same time there is a particle ( $Z$ ) at site  $m$ .  $Z$  is again the same set of states of a site as  $X$  and  $Y$ . Summation over all  $Z$  leads to the exact condition

$$\sum_Z \left( \left[ \begin{array}{c} Y \\ \boxed{X} \\ 1 \end{array} \right] \text{---} Z \right) = \left[ 1 - \frac{\alpha_{l,m}}{z} \right] (XY), \quad (49)$$

with

$$(XY) = \rho^{(2)}(XY) \quad (50)$$

for nearest neighbors.

But the superposition approximation leads to a different value,

$$O_{SA} \left\{ \sum_Z \left( \begin{array}{c} \boxed{X}^Y \\ \boxed{I} \\ \longrightarrow Z \\ m \end{array} \right) \right\} \Rightarrow (XY) \sum_Z C_Z F_{XZ}(I-m) \hat{F}_{XZ}(I-m) W(X, Y). \quad (53)$$

With this correction factor we can now choose all correlation functions as independent variables. This avoids the numerical difficulties described above.

## VI. METHOD OF SOLUTION

The main problem is connected with the solution of an infinite system of nonlinear differential equations for a chosen type of lattice. To solve this problem in practice the following approximation is used. A threshold value  $m_0$  is introduced. For  $m < m_0$  the lattice equations are solved for all nonequivalent points of the lattice (here we use  $m_0 = 5$ ). This first area determines several coordination spheres in which the lattice aspect of the problem is important. In the second area all properties change quasicontinuously with the distance  $|m|$ . Therefore we can use a continuum approximation by introduction of the coordinates  $r = |m|$  and substituting the correlation function  $F(m)$  by the radial one  $F(r)$ . By this substitution the equations transform into nonlinear equations in partial derivatives. As the left (or inner) boundary condition (circumference of the circle with radius  $m_0$ ) the solution within in the first area at  $|m| = m_0$  is used. Because of the weakness of the correlation we can use  $F(\infty) = 1$  as the right (or external) boundary condition. More details of the method of solution are given in Ref. [13].

In our calculation we choose as the initial condition an empty surface  $C_\chi^a(t=0) = 0$  for  $\chi \in \{H, N, A, B\}$ . The activated sites of the catalyst are distributed with  $C_0^a(0) = S$  and  $C_0^b(0) = 1 - S$ , where  $S$  is the mean activity of the surface. The correlation functions are given by

$$\begin{aligned} F_{0000}(I) &= P(0,0)/(1-S)^2 \\ &\equiv 1 + \Gamma(I)/(1-S)^2, \\ F_{0001}(I) &= P(0,1)/[S(1-S)] \\ &\equiv 1 - \Gamma(I)/[S(1-S)], \\ F_{0101}(I) &= P(1,1)/S^2 \equiv 1 + \Gamma(I)/S^2 \end{aligned} \quad (54)$$

where  $P(\sigma, \sigma')$  is defined in Sec. II.

## VII. RESULTS

### A. System behavior for $S = 1$

First we want to study the case in which all surface sites are activated ( $S = 1$ ). This means that a  $N_2$  molecule can adsorb at every pair of free surface sites. Figure 1 represents the behavior of the surface coverages  $\Theta_i$  of the various chemical species  $i$  as a function of the mole fraction of  $N_2$  in the gas phase,  $y_N$ , for the case  $S = 1$  and  $D = 1$ . The most prominent feature in this figure is a kinetic phase transition of second order at  $y_N = y_1 \approx 0.21$ .

For  $y_N < y_1$  the surface is nearly completely covered by H and nearly no reaction takes place. For  $y_N \geq y_1$ ,  $\Theta_H$  drops to zero and the coverages of N, NH, and  $NH_2$  increase. For  $y_N \rightarrow 1$ ,  $\Theta_N$  increases to 0.88, which is the maximum coverage for the adsorption of dimers. The coverages of NH and  $NH_2$  increase rapidly for  $y_N > y_1$  because the composition is nearly stoichiometric on the surface. For larger  $y_N$  these coverages decrease because there are not enough adsorbed H atoms on the surface for their formation (the coverage of N atoms increases). It must be noted that the value of  $y_1$  is very close to the stoichiometric ratio of 0.25 but not identical with it. This difference arises from the small diffusion rate of the H atoms. Therefore the system is not well stirred and adsorbate clusters are formed. This invalidates a description by a mean-field model. The reaction rate is in all cases similar between the stochastic and the CA model. It rises steeply at the phase-transition point and levels off for larger values of  $y_N$ . It is a nonlinear function of  $y_N$ . We do not represent it in the figures.

Figure 2 shows similar data of the surface coverages as in Fig. 1 but now we use a larger diffusion rate of  $D = 10$ . It can be seen that the value of  $y_1$  is shifted to a larger value of  $y_N$  ( $y_1 \approx 0.23$ ), which is closer to the stoichiometric ratio of 0.25. Also, the kinetic phase transition sharpens and it is now nearly of first order. This can easily be understood from the fact that the fast-

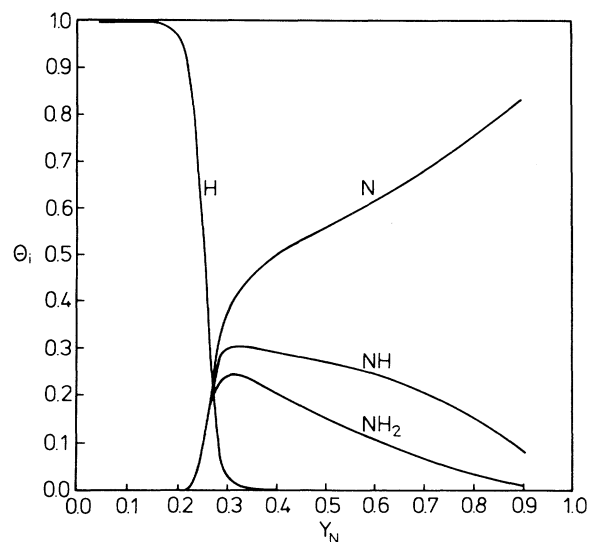


FIG. 1. Phase diagram for the case  $S = 1$  and  $D = 1$ .

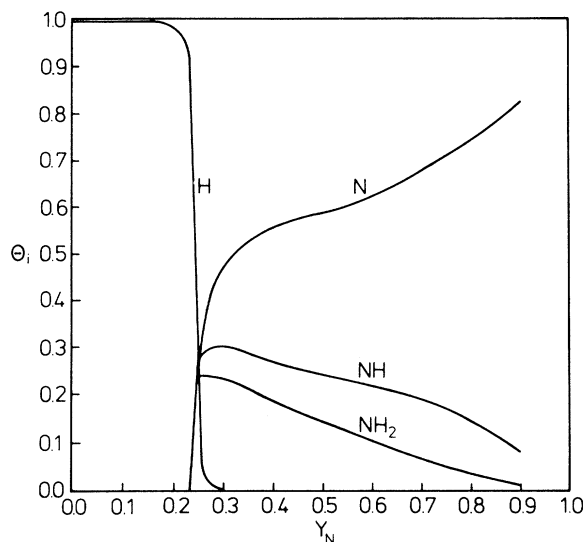


FIG. 2. Phase diagram for the case  $S = 1$  and  $D = 10$ .

moving H atoms react with N, NH, and  $\text{NH}_2$  molecules at the border of the adsorbate clusters. Therefore this system is more of mean-field type. The coverages of NH and  $\text{NH}_2$  are a little bit smaller compared to the case of  $D = 1$ , which shows the more reactive character of the fast-moving H atoms. Just above  $y_1$  the coverage of N is a little bit larger than for the case  $D = 1$ . This arises from the fact that at this point more vacant pairs of surface sites are present which enlarge the probability of the dissociative adsorption of  $\text{N}_2$ .

As an example of a very low diffusion rate we want to study the system behavior for  $D = 0.1$ , which is shown in Fig. 3. For this case the phase transition at  $y_1$  vanishes. Because of the very small reactivity of the H atoms large cluster structures of particles can be formed. This allows

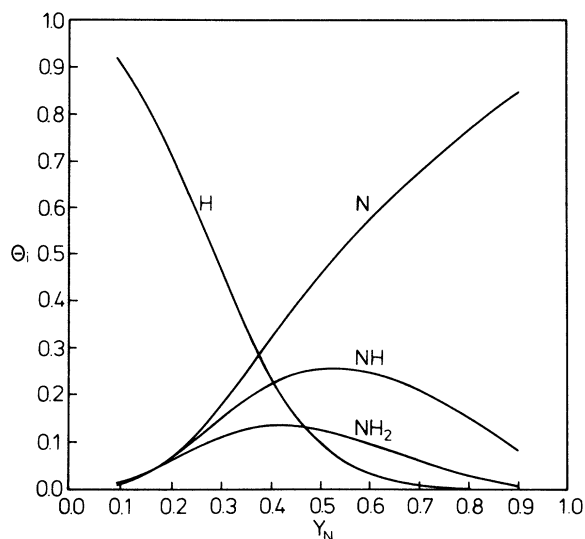


FIG. 3. Phase diagram for the case  $S = 1$  and  $D = 0.1$ .

the simultaneous appearance of H and N atoms on the surface.

### B. System behavior for $S = \frac{1}{8}$

Next we want to study the more realistic case in which not all surface sites are activated. This means a reduction of the adsorption probability of the  $\text{N}_2$  molecules. In the following we assume the case of  $S = \frac{1}{8}$ .

In Fig. 4 the coverages for  $D = 1$  are shown. The kinetic phase transition is of second order and the value of  $y_1$  is shifted to larger values of  $y_N$  compared to the analogous case above. Over the whole parameter range of  $y_N$ ,  $\Theta_H$  is significantly larger than 0.2. The concentrations of N, NH, and  $\text{NH}_2$  increase with increasing  $y_N$  but they are smaller than 0.1. This behavior can easily be understood from the fact that  $\text{N}_2$  molecules can only adsorb on vacant nearest-neighbor pairs from which at least one site must be activated. During the reaction, many activated sites will be blocked via occupation with NH and  $\text{NH}_2$  because reaction occurs by the jump process of H atoms to sites which are covered by N, NH, and  $\text{NH}_2$ . After the reaction the product covers in many cases an activated site. Another process for the blocking of activated sites is the adsorption process of  $\text{H}_2$ , which is very important for small values of  $y_N$ .

If we enlarge the diffusion rate of the H atoms to  $D = 10$  (shown in Fig. 5) the value of the phase-transition point  $y_1$  and the coverages of N, NH, and  $\text{NH}_2$  are nearly unaffected by this change. Only the concentration of H atoms drops more rapidly for  $y_N > y_1$ . This behavior shows the increased reactivity of H atoms which are now more mobile. The coverage of the other particles depend only on the concentration of the activated sites of the surface and not on the reactivity of the H atoms.

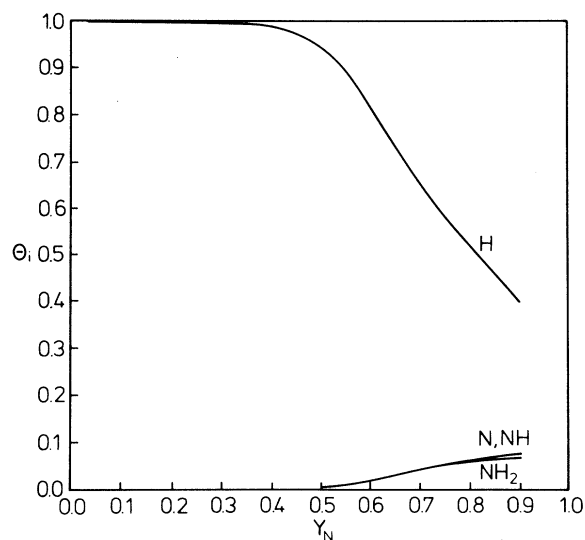


FIG. 4. Phase diagram for the case  $S = \frac{1}{8}$  and  $D = 1$ .



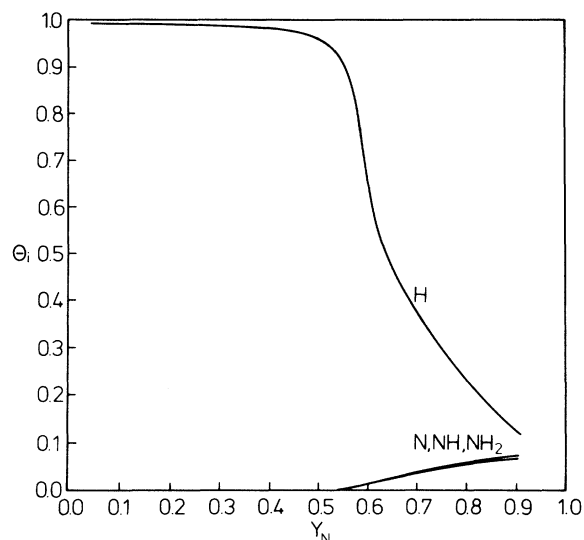


FIG. 5. Phase diagram for the case  $S = \frac{1}{8}$  and  $D = 10$ .

### C. Correlation function

We have also studied the pair-correlation functions of the adsorbed particles which contain a variety of information on the adsorbate structure. In a previously introduced model for the oxidation of CO we have found large O-O and CO-CO correlations, which cause the appearance of oscillations [13]. In contrast to the CO oxidation model a large number (55) of different pair correlations appear in the present reaction model. We observed that all of these are very small with the exception of H-H and N-N correlations between nearest-neighbor sites. This correlation is the result of the dissociative adsorption of the molecules. But within a very short distance (three or four sites) the correlation vanishes. This is clear because of the occurrence of many different pairs which result from the large number of different particles and the state of the surface. In the present model large N cluster cannot appear because of the formation of NH and NH<sub>2</sub> particles during the reaction which immediately breaks off N clusters. The H atoms are distributed randomly over the surface because of their mobility and their large reactivity. For  $S < 1$  the additional effect of randomly distributed active surface sites leads to a random distribution of N<sub>2</sub> adsorption events. Therefore it is clear that in this model large correlations cannot appear. The facts given here present a justification for the statement made following Eq. (22).

## VIII. DISCUSSION

In this paper we have introduced a stochastic model for heterogeneously catalyzed reactions and applied it to the formation of NH<sub>3</sub>. We take into account the occurrence of activated sites for the adsorption of N<sub>2</sub>. For

this system we have previously introduced a CA [2]. The reaction step in the CA model is defined in another way than in the model described here. In the CA model, reaction takes place if two reactive particles are nearest neighbors on the surface. The effect of the diffusion of the H atoms was not included which is in some respect unrealistic. Differences which occur between these two different models are consequences which arise due to the reaction and diffusion events. In the stochastic model reaction occurs by a hopping process of H atoms to sites which are occupied by particles which can react with H atoms. The product is formed on the site to which the H atom hops. This means that in this case the probability to block an activated site is larger in the stochastic model than in the CA model in which the reaction product occupies one of the two sites. This site will randomly be selected. Therefore the probability of the blocking of activated sites is reduced. This results in a larger coverage of N atoms for the case  $S < 1$ .

The reaction models are different in the CA and the stochastic approach because of the so-far unsurmountable difficulties with the nearest-neighbor reaction in the stochastic equations. A detailed investigation of a simple model of the oxidation of CO [13], where diffusion was included in both approaches, lead to the conclusion that the results of the two models are quite close. The CO poisoning of the lattice is of the same order and occurs at the same point. Also, for the oxygen poisoning, the order of the phase transition agrees in the two approaches, but the transition is shifted to a somewhat lower value. But on the whole the agreement is very close. We thus can expect that also in the present model there will be only small changes due to the introduction of the different reaction rule.

For the case  $S = 1$  and  $D = 1$  the results of the stochastic model are in good agreement with the CA model ( $y_1 = 0.262$ ). This is understandable because the different definition of the reaction which leads to a difference in the blocking of activated sites cannot play a role because all sites are activated. The diffusion rate  $D = 10$  leads nearly to the same reactivity as if we define the reaction between nearest-neighbor particles. If the diffusion rate is lowered ( $D = 0.1$ ) the behavior of the system changes completely because of the decrease of the reaction probability. This leads to the disappearance of the kinetic phase transition at  $y_1$  because different types of particles may reside on the surface as nearest neighbors without reaction, a case which does not occur in the CA approach.

The results obtained from the CA model for  $S = \frac{1}{8}$  are in quite good agreement with the results obtained from the stochastic ansatz for  $D = 1$  and 10. Then value of the phase transition point  $y_1$  is found to be  $y_1 \approx 0.4$  in both models. In the stochastic model the density of adsorbed N atoms is smaller compared to the CA model because of the blocking effect of activated sites which arises from the different reaction mechanism.

We have also performed calculations for higher diffusion rates ( $D = 100$ ) and for the triangular lattice (with coordination number  $z = 6$ ). The qualitative

behavior is in complete agreement with the calculation presented here. For the case  $S=1$  the increase of the diffusion rate or the change of the lattice leads to a very small shift of the phase transition point  $y_1$  to higher values of  $y_N$ . This trend is clear because the reactivity of the H atoms is increased by the larger mobility. For  $S < 1$  nearly no effect can be observed, which means that the system behavior is mainly dominated by the number of activated sites. The correlation of the adsorbed particles are rather small as expected for  $S < 1$ .

### IX. CONCLUSIONS

The results obtained with this stochastic model show that surface-reaction systems are well suited for a description via master equations. Because this infinite chain of equations cannot be solved analytically, numerical methods must be used for solving it. In a previous paper we studied the catalytic oxidation of CO over a metal surface with the help of a similar stochastic model. The results are in good agreement with MC and CA simula-

tions. Here we have introduced a much more complex system, which takes the state of catalyst sites and the diffusion of H atoms explicitly into account. Due to this complicated model MC and in some respect also CA simulations cannot be used to study this system in detail because of the tremendous amount of required computer time. The stochastic ansatz offers the possibility to study very complex systems, including the distribution of special surface sites and correlated initial conditions for the surface and the coverages of particles. This model can easily be extended to more realistic models by introducing more aspects of the reaction mechanism. Moreover, other systems can be represented by this ansatz. Therefore this stochastic model represents an elegant alternative to the simulation of surface reaction systems via MC or CA simulations.

### ACKNOWLEDGMENTS

This research was supported by the Deutsche Forschungsgemeinschaft and in part by the Fonds der Chemischen Industrie.

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