

Effects of ER process on the phase diagram of an A-B₂ surface reaction

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1994 J. Phys. A: Math. Gen. 27 L651

(<http://iopscience.iop.org/0305-4470/27/18/002>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.68

The article was downloaded on 01/06/2010 at 21:40

Please note that [terms and conditions apply](#).

LETTER TO THE EDITOR

Effects of ER process on the phase diagram of an A–B₂ surface reaction

Botao Zhang† and Hui-yun Pan‡

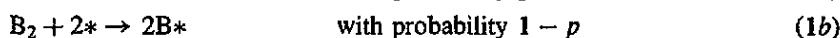
† Physics Group, Information and Engineering Institute, Zhengzhou 450 002, People's Republic of China

‡ Chemistry Department, Zhengzhou University, Zhengzhou 450 052, People's Republic of China

Received 16 May 1994

Abstract. We generalize the A–B₂ surface reaction model of ZGB to include the Eley–Rideal process, and introduce a 'partial simulation' method for computer simulations. Numerical results show that the second-order phase transition disappears when the ER process takes part in the kinetics.

A few years ago Ziff, Gulari and Barshad introduced a non-equilibrium kinetic lattice model (ZGB model) to study the A–B₂ surface reactions [1]; in contrast to the classical approach with rate equations, this model takes into account fluctuations and spatial correlations of the surface reaction species, and hence it shows complex dynamic behaviour of the system, in spite of its simple formulation. An A–B₂ surface reaction in the ZGB model can be formulated as follows:



where * represents a vacant site on the surface, 2* represents a nearest * pair, and A* and B* represent different adsorbed atoms on the surface. In the primitive form of this model, diffusion, desorption of reactants, and thermal effects are ignored and the kinetics are assumed to be adsorption limited with the reaction probability equalling unity.

Simulations of the ZGB model using the Monte Carlo method show that the A–B₂ reaction system exhibits three phases: the A-saturated, the B-saturated and the reactive phase. For $p < p_1 \simeq 0.3907$ [9], the surface is eventually saturated with B, for $p > p_2 \simeq 0.52560$ [10], it is saturated with A, while for $p_1 < p < p_2$, the system remains in a steady state with reaction continuing indefinitely, where p is the mole fraction of component A in the gas phase above the surface. The phase transition at point p_1 is second order because at this point the coverages of A and B vary continuously with p , while the transition at point p_2 is first order because the coverages vary discontinuously.

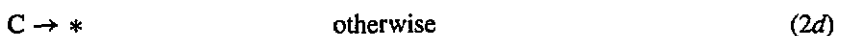
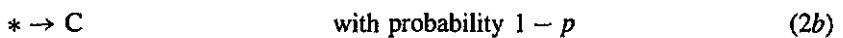
Lately, the ZGB model had been studied by some other methods and modified in different ways, for example, Dickman [2] developed a mean-field cluster method in which site and pair approximations were considered, Chopard and Droz [3] (CD) introduced a cellular

automaton version (CA) of the ZGB model, in which a conditional occupied state C is added to the three states (*, A*, B*) to approximate the requirement for B-adsorption. Moreover, works have been reported in which the ZGB model for finite reaction rates [4, 5], or including species A desorption [6] are considered.

It should be noted that usually calculations have been done on the assumption that the Langmuir-Hinshelwood (LH) process is the only process active in the kinetics, i.e. only the adsorbed atoms A* and B* can react, but experiments suggest that, in general, the LH process is not the only process in A-B₂ surface reactions. As an example [7], for the oxidation of SO₂ on certain catalytic surfaces the Eley-Rideal (ER) process may play a part in the kinetics. That is, an atom A in the gas phase may strike an adsorbed B* and react with it. The question is, how the ER process affects the kinetics of the A-B₂ surface reaction or how the phase diagram varies when the ER process takes part in this reaction? This problem will be discussed later in this letter. This letter is organized as follows. Firstly, a modified ZGB model including the ER process is proposed and a simulation method, namely 'partial simulation' (PS) is introduced. Next the results of simulation are given. Finally, the results are discussed and the PS method is commented on.

The model and the method

The model considered is similar to the CD version of the ZGB model. The surface is modelled as a square lattice, each site of which can be in one of four different states: empty *, A-occupied A*, B-occupied B* or a conditionally occupied state C. A molecule A strikes the lattice with a probability p and can be adsorbed by a * (an empty state * on the lattice becomes A* with probability p); a molecule B₂ strikes the lattice with probability $1 - p$ (an empty state * becomes C with probability $1 - p$), and can be adsorbed only by a nearest-neighbour C pair (only adjacent C pairs become B* states). If an A* and a B* are nearest neighbours, they react and desorb immediately, at the same time two *'s are generated on the surface (LH process). If a molecule A in the gas phase strikes a B*, they react with probability r and desorb immediately, while an a* is generated (ER process). We assume the LH process is prior to the ER process, and the gas above the surface is continuously replenished to keep p constant. The steps of the model can be summarized as follows:



Let N , N_0 , N_A , N_B and N_C represent the numbers of total lattice sites, *, A*, B* and C states, respectively ($N_0 + N_A + N_B + N_C = N$), N_{AB} and N_{CC} represent the numbers of A*B* pairs and CC pairs, respectively. Then we can write the relations between these numbers of time-step t and that on time-step $t + 1$ as follows:

$$N'_0 = 2N_{AB} + N_C - N_{CC} + (N_B - N_{AB})pr \quad (3)$$

$$N'_A = N_A + N_0p - N_{AB} \quad (4)$$

$$N'_B = N_B + 2N_{CC} - N_{AB} - (N_B - N_{AB})pr \quad (5)$$

$$N'_C = N_0(1 - p) \quad (6)$$

where all quantities with a prime refer to time evolution step $t+1$, and the term $(N_B - N_{AB})pr$ represents the effect of the ER process, $r = 0$ means that only the LH kinetics are to be considered.

We carry out the simulations of the two-site processes to obtain N_{AB} and N_{CC} , which reflect the spatial correlations of surface reaction species. Positions of all lattice sites are labelled by integer numbers from 0 to $N - 1$. At each time step when N_A , N_B and N_C have been found from (3)–(6), a 'random number generator' generates N_A , N_B and N_C random integer numbers on $[0, N - 1]$, respectively. The positions of A*, B*, and C states are modelled as these three random integer number sequences, then N_{AB} and N_{CC} are calculated with a computer.

Note that in the CD model the CA rules are not stoichiometric, as first pointed out by Ziff *et al* [8], for example, a neighbouring triplet B*A*B* is allowed to react and desorb, and a CCC is allowed to become a B* B* B*. This situation does not occur in our calculations, since stoichiometry is taken into account in the process of our simulations.

Results

Simulations have been carried out on an $N = 64 \times 64$ lattice with periodic boundary conditions and initial values: $N_0 = N$, $N_A = N_B = N_C = 0$. The average coverage fractions $\theta_A = N_A/N$ and $\theta_B = N_B/N$ are obtained when the system has reached a steady state. Generally, 300–2000 time steps are needed to reach such a state. For $r = 0$ (the LH process is the only process considered), the phase diagram is shown in figure 1. For $p < p_1 = 0.315 \pm 0.005$, the system is saturated with B, and for $p > p_2 = 0.389 \pm 0.001$, the system is saturated with A, while for $p_1 < p < p_2$, the system goes into a reactive steady state. At the point p_1 the phase transition is second-order, while at the point p_2 the transition is first-order. The results are consistent with the Monte Carlo results of ZGB model [1].

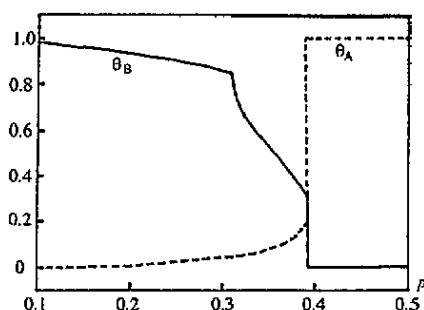


Figure 1. The phase diagram for $r = 0$. The full curve represents the coverage fraction θ_B , the broken curve represents the coverage fraction θ_A .

It should be noted that for the B-saturated phase there still remains a certain fraction of empty sites, it may be related to the fact that some correlations (for example between $N_{AB}(t)$ and $N_{CC}(t + 1)$) were ignored in our simulations. Further investigations are in progress.

For $r \neq 0$, the coverage fraction curve $\theta_A(p, r)$ is nearly identical to that of $\theta_A(p, 0)$. On the other hand, the coverage fraction curve of $\theta_B(p, r)$ is very different from that of $\theta_B(p, 0)$. The first-order phase transition value p_2 decreases slightly with increasing r , while no second-order transition can be found with r decreasing to as small as 0.001. Figure 2

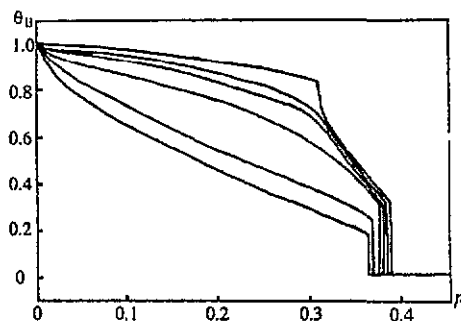


Figure 2. The phase diagram for $r \neq 0$. The curves represent $\theta(p, r)$ corresponding, from top to bottom, to $r = 0, 0.001, 0.01, 0.1, 0.5$ and 1 respectively.

shows the curves $\theta_B(p, r)$ corresponding to, from top to below, $r = 0, 0.001, 0.01, 0.1, 0.5$ and 1 , respectively.

Discussions

For the $A-B_2$ surface reaction model, the second-order phase transition disappears when the ER process takes part (even a very small part) in the kinetics, the B-saturated phase gives way to the reactive phase. This can be understood as follows. For the pure LH kinetics, when the probability p is decreased below the critical value p_1 , the B-adsorption rate is greater than the A's, and more and more B* will occupy the surface until the B-saturated phase appears. However, if the ER process also takes part in the kinetics, in the region $0 < p < p_1$ some vacant sites will be produced due to the reactions of $A+B^*$. Because these vacant sites are mostly single, they cannot be reduced in number by the B-adsorption. Thus more and more vacant sites will be produced at the following steps until the reactive phase appears.

It is also necessary to comment on the PS method. In the PS method one only carries out simulations of the microscopic processes of interest, some irrelevant correlation effects are averaged out by means of (3)–(6) given in section 2, so the PS method is superior in simplicity to the ordinary simulation method without significant loss in accuracy. With this method one can obtain the phase diagram of an $A-B_2$ surface reaction system which is qualitatively the same as that from Monte Carlo simulations with much less work. Moreover, this method may easily be adapted to different problems, as shown in this letter.

It should be noted that, after this letter was completed, our attention was called to a related paper by Meakin [11], in which ER processes were taken into account in the ZGB model of CO surface oxidation and similar results to ours were obtained. However, in contrast to Meakin's work, in our letter we use the cellular automaton (CA) version of the ZGB model and propose a new simulation method, the merit of which we have shown. Besides, for the two-dimensional case considered here, we consider the $A-B_2$ surface reaction with an adjustable parameter r characterizing the efficiency of the ER process in the reaction—the topic studied by Meakin is a special case of the ER process with $r = 1$.

We are grateful to a referee for calling attention to a related paper by Meakin. We also thank Professor Zousen Zhao for many helpful discussions and acknowledge support from the National Natural Science Foundation of China and the Natural Science Research Foundation of Henan Province.

References

- [1] Ziff R M, Gulari E and Barshad Y 1986 *Phys. Rev. Lett.* **56** 2553
- [2] Dickman R 1986 *Phys. Rev. A* **34** 4246
- [3] Chopard B and Droz M 1988 *J. Phys. A: Math. Gen.* **21** 205
- [4] Considine D, Takayasu H and Redner S 1990 *J. Phys. A: Math. Gen.* **23** L1181
- [5] Kohler J and ben-Avraham D 1992 *J. Phys. A: Math. Gen.* **25** L141
- [6] Brosilow B J and Ziff R M 1992 *Phys. Rev. A* **46** 4534
- [7] Halstead J A *et al* 1990 *J. Phys. Chem.* **94** 3261
- [8] Ziff R M, Fichtorn K and Gulari E 1991 *J. Phys. A: Math. Gen.* **24** 3727
- [9] Jensen I, Fogedby H C and Dickman R 1990 *Phys. Rev. A* **41** 3411
- [10] Ziff R M and Brosilow B J 1992 *Phys. Rev. A* **46** 4630
- [11] Meakin P 1990 *J. Chem. Phys.* **93** 2903