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Monte Carlo Simulation of a Bimolecular Reaction of the Type $A + (1/2)B_2 \rightarrow AB$ – The Influence of A-Desorption on Kinetic Phase Transitions

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Abstract. The model recently proposed by Ziff et al. [1] for reactions of the type $A+(1/2)B_2 \rightarrow AB$ is extended in order to study the effect of A-desorption on irreversible (kinetic) phase transitions (IPT). The IPT from a stationary state with AB-production to a B-poisoned state is not influenced by A-desorption. On the other hand, desorption of A-species prevents the existence of a truly A-poinsoned state. Therefore the IPT from the stationary regime to an A-poisoned state does not occur but an apparent phase transition is observed for small values of the desorption probability (P_D). The rate of AB-production (R_{AB}) crosses over from a regime where it becomes dominated by the rate of A-adsorption, when the coverage with A-species is negligible to another regime where R_{AB} is dominated by the rate of B_2-adsorption, when the coverage with B-species is negligible. Within the former regime, R_{AB} decays exponentially with the mole fraction of A-molecules in the gas phase and exhibits a power law dependence with P_D (exponent $\gamma = 2$).

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The kinetic of recombination processes has been extensively studied by means of virtually all available experimental and theoretical techniques. This task is motivated by scientific interest and practical applications in many fields related to physics, chemistry and biology. Within this context, kinetic or irreversible phase transitions (IPT) occurring in recombination reactions have recently received growing attention [1–18] after the model proposed by Ziff et al. (ZGB) [1]. The ZGB model may be applied to the catalytic oxidation of carbon monoxide in particular or to bimolecular reactions of the type $A + (1/2)B_2 \rightarrow AB$ in general. The ZGB model [1–18] basically retains the adsorption–desorption selectivity rules of the Langmuir-Hinshelwood mechanism, it has no energy parameters, and the only independent variable is p_A, namely the mole fraction of A in the gas phase. Obviously, these crude assumptions imply that, for example, diffusion of adsorbed species is neglected, desorption of the reactants is not considered, lateral interactions are ignored (for a study of the effects of correlations between reactants on adsorption–reaction processes see for example [19, 20]), etc. For details on the ZGB model see [1–18]. Nevertheless, a major interest in the ZGB models is due to the existence of two IPT's from a stationary state with AB-production to poisoned states with A and B particles, respectively. These transitions become apparent in Fig. 1, where the coverage with $A(\vartheta_A)$ and $B(\vartheta_B)$ particles as well as the rate of AB-production (R_{AB}) are plotted against p_A. For $p_A \leq p_{AB}(p_A \geq p_{AA})$ the system becomes poisoned with $B(A)$ particles, while a reaction window is found for $p_{AB} < p_A < p_{AA}$, where p_{AA} and p_{AB} are critical probabilities.

The aim of this work is to study, by means of the Monte Carlo simulation technique, the effect of A-desorption in the predictions of the model, so let us denote by ZGBD the ZGB model with A-desorption. Due to this additional asumption one has to introduce a second parameter in the model, namely the desorption probability P_D, $0 \leq P_D \leq 1$) of A-particles. Therefore, the ZGB model is recovered for $P_D = 0$. The assumption of A-desorption is motived by the fact that, in most surfaces, the first order desorption of CO (i.e. CO $\equiv A$) takes place at a much lower temperature than the second order (recombinative) desorption of O_2 (i.e. $O_2 \equiv B_2$). On the other hand, one has to recognize that surface diffusion, particularly of CO, may be appreciable within the range of temperatures, where desorption occurs. Nevertheless, in previous works [9, 10, 17, 21] it has been demonstrated that surface diffusion of A-particles does not substantially influence the predictions of the ZGB model. In fact, the only remarkable effect is the shift of the critical probability for the occurrence of A-poisoning from

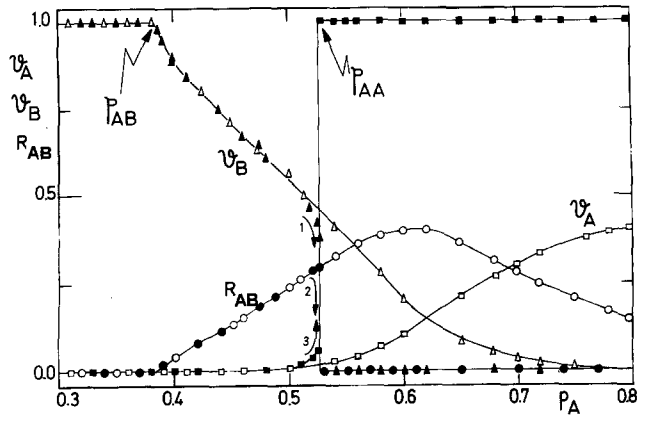

Fig. 1. Plots of the coverages $\vartheta_A(\vartheta_B)$ with $A(B)$ particles and the rate of AB-production (R_{AB}) vs p_A for both the ZGB $P_D = 0$, filled symbols) and the ZGBD (in this case $P_{D=1}$, empty symbols) models, respectively. $p_{AB} \cong 0.3834$ and $p_{AA} \cong 0.5261$ are critical probabilities at which the IPTs of the ZGB model take place. The arrows 1, 2 and 3 shown the abrupt changes in $\vartheta_B \rightarrow 0$, $R_{AB} \rightarrow 0$ and $\vartheta_A \rightarrow 1$ characteristic of the ZGB model at the first order IPT at p_{AA}. More details in the text

$p_{AA} \cong 0.5261$ to $p^*_{AA} \cong 0.540$ [21]. Therefore, in order to save computing time, without loosing generality, it is convenient to simulate the ZGBD model without diffusion.

1 The ZGBD Model and the Simulation Method

The Monte Carlo simulation method applied to the ZGB model has been described in detail in previous work [1, 3, 6, 9, 10, 14–17], so it does not need to be repeated here. The simulations are performed on the square lattice of size $L \times L$ assuming periodic boundary conditions. While the ZGB model assumes the irreversible adsorption of A molecules, in the ZGBD model such molecules have a finite probability (P_D) to desorb. So, within the Monte Carlo simulation [1, 3, 6, 9, 10, 14–17], one has to follow the ZGB algorithm if a randomly selected site is empty or occupied by a B-atom. Otherwise, if that site is occupied by an A-molecule a random number ($0 < R < 1$) has to be generated and compared with P_D: if $R \leq P_D$, A is desorbed and the site becomes empty, if $R > P_D$ the trial ends. The same algorithm for the ZGBD model has also been employed by Ehsasi et al. [10]. Note that the choice of this algorithm implies that we have restricted ourselves to the case $P_D \leq p_A + p_B = 1$. Nevertheless, this shortcoming is not essential for the purpose of the present work because the most interesting behavior of the ZGBD model can be studied without difficulties in spite of the mentioned limitation, as it follows from the results and their discussion presented in the next section.

The Monte Carlo simulations are performed in a multitransputer system with five T-800 processors. The algorithms are developed in OCCAM 2 [22], including the random number generator [23]. Simulations on small lattices ($L \leq 40$) are performed in a IBM 3032 processor with algorithms written in FORTRAN 77.

2 Results and Discussion

In order to acquaint the reader with the relevant predictions of the ZGB model and to remark their differences with the ZGBD model, Fig. 1 shows the coverage $\vartheta_A(\vartheta_B)$ with $A(B)$ particles, respectively, and the rate of AB-production versus p_A for both models. Note that filled (empty) symbols correspond to the ZGB (ZGBD) model, respectively. From Fig. 1 it follows that the critical probability p_{AB}, at which the IPT from the steady state with AB-production to the B-poisoned state occurs, is the same for both models. Therefore, this point does not merit further study since it is well understood [1, 3, 6, 14, 16, 21]. On the other hand, for $p_A \geq p_{AA}$ the differences between the models become apparent. While the ZGB model exhibits a first order IPT with abrupt changes of the relevant properties, namely $\vartheta_B \rightarrow 0$, $\vartheta_A \rightarrow 1$ and $R_{AB} \rightarrow 0$, the ZGBD model (for this particular case $P_D = 1$) shows smooth changes of the reactant's coverages and the rate of AB-production.

Figure 2 shows the dependence of the rate of AB-production on p_A, for different values of $P_D (5 \times 10^{-3} \leq P_D \leq 1)$. Let us recall that, in the ZGB model, just at $p_{AA} \cong 0.5261$ one has a first order kinetic transition from the stationary regime with AB-production (for $p_A < p_{AA}$) to a poisoned state (without AB-production) with A-particles (for $p_A \geq p_{AA}$). From Fig. 2 it follows that the ZGBD model exhibits an "apparent phase transition" behavior very close to p_{AA} for $P_D \leq 0.01$, that is a drastic drop in R_{AB} (about of 2–3 orders of magnitude) is observed. For $P_D = 0.05$, R_{AB} also decreases abruptly (about of one order of magnitude) but slightly above p_{AA}. From Fig. 2 it follows that for $P_D > 0.1$ the "apparent phase transition" behavior is not observed any more in the sense that R_{AB} does not exhibit a drastic drop when p_A is slightly increased. Therefore, the

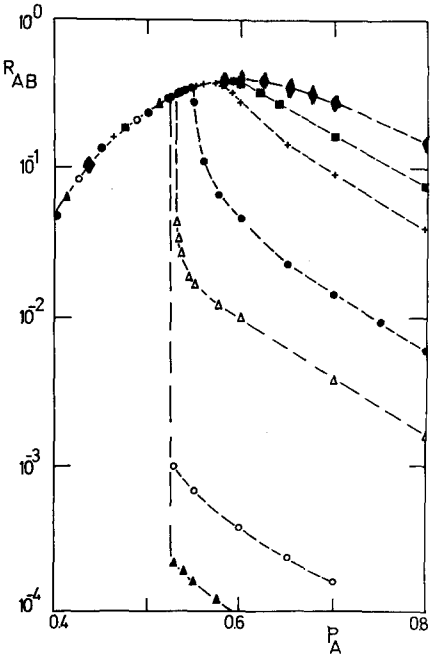

Fig. 2. Semi-logarithmic plot of R_{AB} vs p_A for different values of P_D (▲: 0.005; ○: 0.01; △: 0.05; ●: 0.10; +: 0.30; ■: 0.50; ◆: 1.00) ($5 \times 10^{-3} \leq P_D \leq 1$). Simulations performed on lattices of size $L = 128$

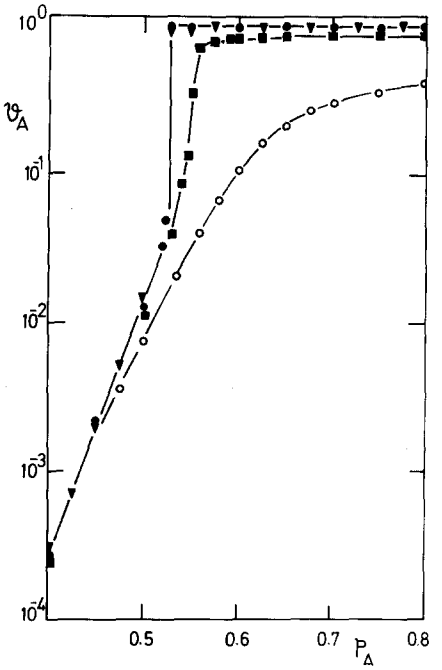

Fig. 3. Semi-logarithmic plot of ϑ_A vs p_A for different values of P_D (o: 1.000; ■: 0.100; ▼: 0.010; •: 0.005) ($5 \times 10^{-3} \leq P_D \leq 1$). Simulations performed on lattices of size $L = 128$

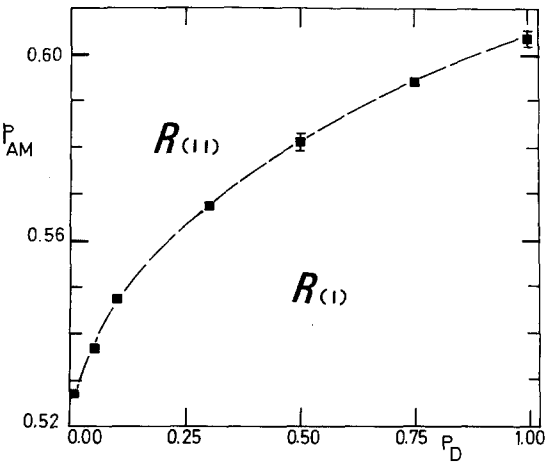

Fig. 4. Plot of the value of p_A at the maximum of $R_{AB}(p_{AM})$ vs P_D. The dashed line, drawn to guide the eyes, represents the border between regions I and II where the reaction has two different regimes, as discussed in the text

crossover from the regime with absence of phase transition to that showing the "apparent phase transition" behavior lies close to $P_D \cong 0.1 \pm 0.05$. Since in Monte Carlo simulations phase transitons are shifted and rounded off by finite-size effects, a more precise determination of the crossover region should require a detailed finite-size scaling analysis which is beyond the aim of the present work. Also, since the crossover from one regime to the other is not abrupt, even extensive simulations may not be useful in order to obtain further insight on this issue. It is also interesting to note that R_{AB} becomes independent of P_D for $p_A < p_{AA}$. The whole behavior of R_{AB} is consistent with the dependence of ϑ_A on p_A shown in Fig. 3. In fact, for $p_A < p_{AA}$, ϑ_A is very small ($\vartheta_A < 5 \times 10^{-2}$) and therefore the effect of P_D on R_{AB} is negligible. On the other hand, the "apparent phase transition" behavior of R_{AB} for $P_D \leq 0.05$ is due to the fact that the surface remains almost completely poisoned with A-particles ($p_A > p_{AA}$).

The influence of reactants' desorption on the predictions of the ZGB model has also been studied by Fischer and Titulaer [7] by means of mean field and Bethe-Peierls approximations. For this purpose they have introduced two additional parameters, namely D and E which are the rate constants for A and B_2 desorption, respectively [7]. They have found that when D and/or E becomes too large, the model no longer has phase transitions [7]. Now, addressing our attention to the IPT close to p_{AA} they have reported that for small values of D and E the reaction rate in the state of high ϑ_A is negligible, thus the state is considered as "effectively poisoned" [7]. These findings are in good qualitative agreement with the Monte Carlo results of the present work. In fact, as discussed above (see also Fig. 2), for small values of P_D one has a dramatic drop in the rate of AB production and ϑ_A approaches to one (see Fig. 3). This result can be, using a somewhat arbitrary criterion, identified either as an "effectively poisoned state", like in [7], or as an "apparent phase transition", like in the present work, since strictly speaking a truly poisoned state can no longer exist for finite values of P_D (or D in [7]). On the other hand, from the mean field equations of motion used in [7], one expects a small, but finite, dependence of ϑ_A on P_D even below p_{AA}. This dependence is also confirmed by the Monte Carlo results shown in Fig. 3. In fact, while for very small values of $P_D (P_D \leq 0.01)$ and far below p_{AA} Monte Carlo data are somewhat scattered, close to p_{AA} it becomes clear that ϑ_A decreases when increasing P_D, as expected. Furthermore, the effect of B-desorption on the ZGB model has also been studied by Kaukonen et al. [9] and Ehsasi et al. [10] by means of computer simulations and, in the former, also experimentally. In both cases, the authors did not go into nearly the detail of investigation than in the present work, but it is worth mentioning that their Monte Carlo results [9, 10] are in excellent qualitative agreement with those shown in Figs. 1–3.

Figure 2 also shows that the different plots of R_{AB} as a function of p_A exhibit maxima (at p_{AM}) which depend on P_D as it is shown in Fig. 4. In other words, the major efficiency of AB-production is achieved for the set of values of the parameters of the model (p_A, P_D) which defines the curve of Fig. 4. Also, this curve divides the plane (p_A, P_D) in two regions (region I and II in Fig. 4) characterized by quite different reaction regimes.

Let us first discuss the observed regime within region I. Since ϑ_A is almost negligible (see Figs. 1 and 3) it is natural to assume tht the rate of A-adsorption ($R_{A\,\mathrm{Ad}}$) should equal the rate of AB-production. Also, due to the fact that A-particles require a single adsorption site, R_{AB} has to be proportional to both p_A and the probability to find an empty site, i.e. $(1 - \vartheta_A - \vartheta_B)$, so

$$R_{AB} \propto p_A(1 - \vartheta_A - \vartheta_B) \cong p_A(1 - \vartheta_B) . \quad (1)$$

Figure 5 shows that (1) nicely holds within region I. Also, let us recall that this regime is independent of P_D (Figs. 1 and 2).

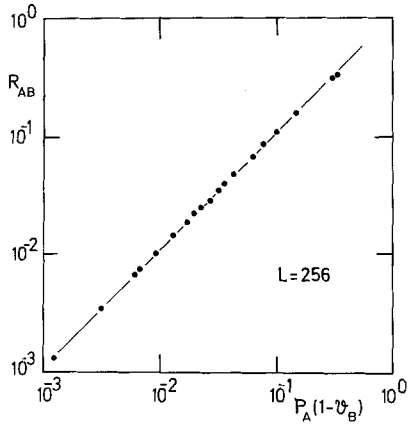

Fig. 5. Log–log plot of the rate of AB-production (R_{AB}) vs $p_A(1-\vartheta_B)$ for ($p_A < p_{AM}$)

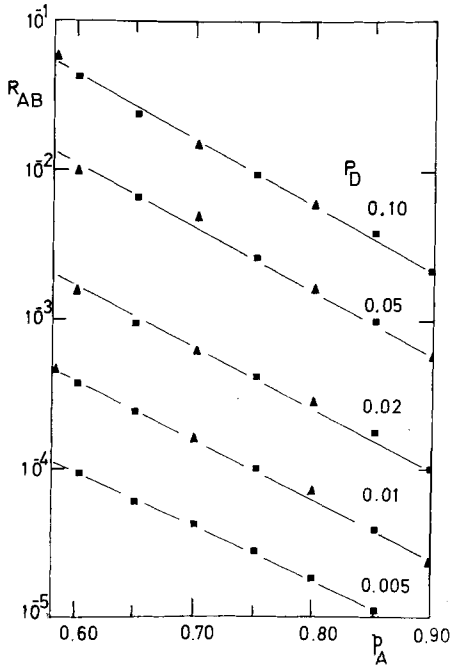

Fig. 6. Semi-logarithmic plot of the rate of AB-production (R_{AB}) vs $p_A(p_A > p_{AM})$ for different values of the desorption probability P_D (■: $L = 128$; ▲: $L = 40$)

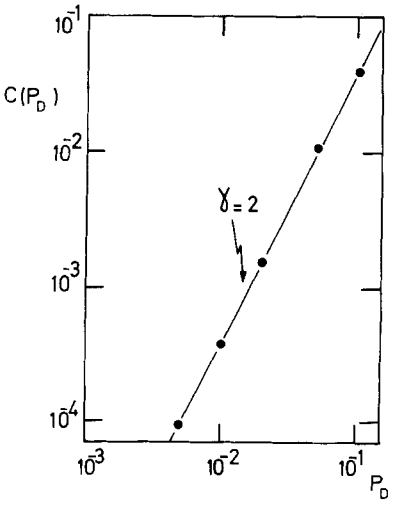

Fig. 7. Log–log plot of the intercept $C(P_D)$ of the straight lines of Fig. 6 at $p_A = 0.60$ vs P_D. The straight line has slope $\gamma = 2$

Pointing now our attention to the reaction regime within region II, Fig. 6 shows semi-log plots of R_{AB} vs p_A for $p_A > p_{AA}$ obtained for different values of P_D. The obtained straight lines strongly suggest that the following behavior should hold

$$\ln R_{AB} = C(P_D) + S p_A \,, \tag{2}$$

where the slope S is almost independent of both p_A and P_D, while the intercept $C(P_D)$ clearly depends on P_D. Also, data corresponding to lattices of different size $L = 40$ and $L = 128$ show that finite-size effects are negligible. The slopes and the intercepts have been evaluated by least-squares fitting of the straight lines of Fig. 6. The average value of the slopes is $S \cong -9.07 \pm 0.7$ while a log–log plot of $C(P_D)$ vs P_D (Fig. 7) exhibits a straight line behavior with slope $\gamma = 2$. Summing up, one has that (2) can be rewritten as

$$R_{AB} \propto P_D^{\gamma} \exp(S p_A) \begin{cases} \text{with} & \\ \gamma = 2\,, & S \cong -9.0\,, \\ p_A > p_{AA}\,, & P_D < 0.2\,. \end{cases} \tag{3}$$

The crossover from the behavior characteristic of region I to that one of region II becomes nicely apparent in log–log plots of R_{AB} vs P_D with p_A as parameter (Fig. 8). In fact, for $p_A < p_{AA}$ one has that R_{AB} is independent of P_D while for $p_A > p_{AM}$ the obtained straight line behavior with slope $\gamma = 2$ is in agreement with the results shown in Fig. 7. It is interesting to note the abrupt crossover, which corresponds

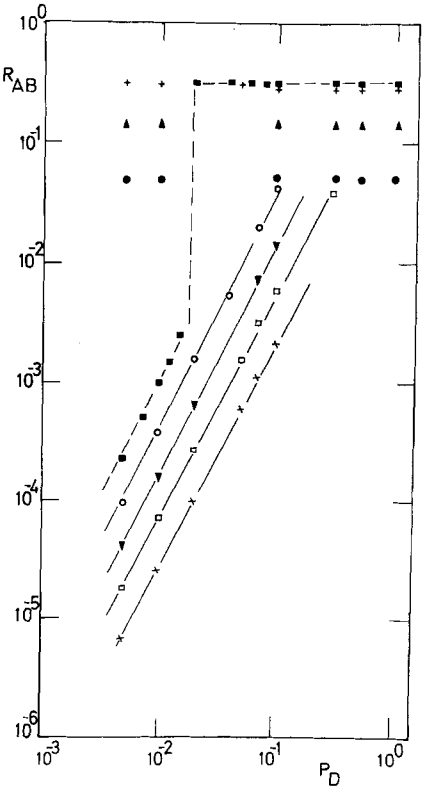

Fig. 8. Log–log plot of the rate of AB-production (R_{AB}) vs the desorption probability (P_D) for different values of p_A (•: 0.40; ▲: 0.45; +: 0.525; ■: 0.53; ○: 0.60; ▼: 0.70; □: 0.80; ⌁: 0.90). The dashed line, for $p_A = 0.53$, has been drawn to guide the eyes and it shows the cross over from the regime characteristic for $p_A < p_{AM}$ to that for $p_A > p_{AM}$ close to $P_D \cong 1.5 \times 10^{-2}$. The full straight lines, for $p_A \geq 0.60$, have slopes $\gamma = 2$. More details in the text

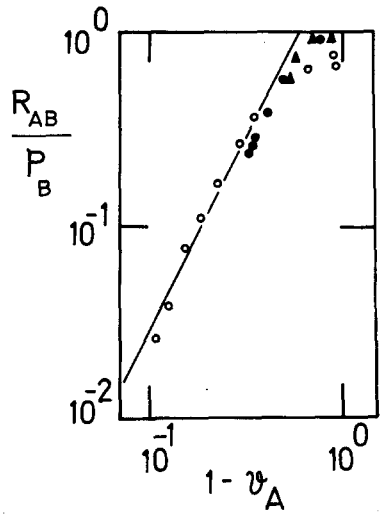

Fig. 9. Log–log plot of R_{AB}/p_B vs $1-\vartheta_A$) for different values of P_D (○: 0.1; ●: 0.5; ▲: 1.0). The straight line has slope 2

to the change of the regime from region I to region II in Fig. 4, observed for $p_A = 0.53$ close to $P_D \cong 1.5 \times 10^{-2}$ which is shown by the dashed line in Fig. 8.

On the other hand one can also study the dependence of R_{AB} on the surface coverage within region II. Since ϑ_A is close to 1 (except for $P_D \to 1$) it is natural to assume that R_{AB} should equal the rate of B_2-adsorption ($R_{B\,Ad}$), but now due to the requirement of two nearest-neighbor (n–n) empty sites for this adsorption process, one expects that $R_{B\,Ad} \propto p_B(1-\vartheta_A-\vartheta_B)^2$. So, remembering that $p_A + p_B = 1$, it follows

$$R_{AB} = (1-p_A)(1-\vartheta_A-\vartheta_B)^2\,, \tag{4a}$$

$$R_{AB} \cong (1-p_A)(1-\vartheta_A)^2\,, \qquad \vartheta_B \to 0\,. \tag{4b}$$

Figure 9 shows a log–log plot of R_{AB}/p_B vs $(1-\vartheta_A)$ and the obtained straight line with slope 2 confirms the validity of (4b). Nevertheless, it should be recognized that the data of Fig. 9 are somewhat more scattered than those of Fig. 5. So, let us recall the assumption that the probability to find two empty n–n sites is given by $(1-\vartheta_A-\vartheta_B)^2$ holds for a random distribution of empty sites. But, in the present case one should expect the existence of correlations between empty sites because they are generated by pairs for the desorption–reaction process [13], so these correlations may cause the observed scattering of the data.

3 Conclusions

The effect of A-adsorption on the predictions of the ZGB model for bimolecular reactions of the type $A + (1/2)B_2 \to AB$ is studied by means of the Monte Carlo simulation method. It is shown that the IPT from a reactive state with AB-production to the poisoned state with B-particles is not affected by A-desorption. While, desorption of A-species prevents the existence of a truly A-poisoned state, an "apparent phase transition" behavior is observed close to p_{AA}, in the sense that, the rate of AB-production abruptly decreases and ϑ_B approach unity provided that $P_D \leq 0.05$. For $P_D > 0.10$ smooth variations of the coverages with the reactants and R_{AB} are observed. In all cases R_{AB} exhibits a maximum at p_{AM} which depends on P_D. Close to p_{AM} the rate of AB-production crosses over from a regime where it becomes dominated by the rate of A-adsorption, when the coverage with A-species is negligible ($p_A < p_{AM}$), to another regime where R_{AB} is dominated by the rate of B_2-adsorption, when the coverage with B-species is negligible ($p_A > p_{AM}$). It is also found that for the former regime, R_{AB} decays exponentially with p_A and has a power law dependence with P_D (exponent $\gamma = 2$).

We expect that the present work will contribute to understand the effect of reactant desorption on the ZGB model. In order to overcome another shortcoming of the model, the study of the influence of lateral interactions on the IPT is in progress.

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