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COMMENT

Comment on ‘Irreversible saturation transitions in dimer–dimer reaction models of heterogeneous catalysis’

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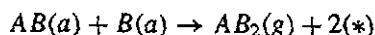
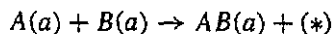
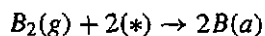
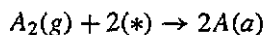
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Abstract. We report results of a Monte Carlo study of the irreversible dimer–dimer reaction ($A_2 + B_2$) on a square lattice. We study the three possibilities for which the probability of formation of AB (adsorbed) is greater than, equal to or less than the formation of AB_2 (gas). For the entire range of partial pressures (p) of B_2 in the gas phase the lattice is poisoned by a combination of A and AB . At $p = \frac{2}{3}$ an irreversible phase transition is observed. For $0 < p < \frac{2}{3}$ the coverages depend on the choice of formation probabilities of AB and AB_2 .

Recently Albano [1] has reported results of a Monte Carlo study of the irreversible dimer–dimer (DD) reaction on a square lattice. We have been carrying out a study of this reaction, using a model identical to the one described by him. While our results predict an irreversible phase transition (IPT) for the model M_1 (where no diffusion and no desorption of the dimer B_2 is allowed) at $p = \frac{2}{3}$ (where p is partial to pressure of B_2 in the gas phase), in agreement with the results of Albano we obtain coverages for A and AB which do not agree with those reported by him.

The model that we have studied corresponds to that of Albano’s for the case when diffusion as well as the reassociation and consequent desorption of the two species is ignored (M_1 model). The model reaction proceeds according to the Langmuir–Hinshelwood reaction mechanism.



where $(*)$ denotes a vacant site while (a) and (g) denote adsorbed and gas phases.

The simulation of this process is performed on a square lattice with periodic boundary conditions. Different processes involved in the simulation are the following. (i) A surface site is chosen at random, if it is already occupied the trial ends, otherwise (ii) a neighbouring surface site is also picked up at random. If this site is occupied the trial ends (iii) in case both the sites are vacant one of the two molecular species, i.e. B_2 or A_2 is picked with a probability P or $(1 - P)$ respectively. This is then adsorbed onto the two empty sites in its atomic form. (iv) In case A_2 happens to be adsorbed, the six nearest neighbouring (NN)

sites of the two $A(a)$ atoms are scanned randomly for the presence of a $B(a)$ atom. If a single $B(a)$ atom is found, $A(a)$ reacts with $B(a)$ to form $AB(a)$. $B(a)$ atom vacates its site and moves to the site occupied by the $A(a)$ atom. If two $B(a)$ atoms are found, $A(a)$ reacts with these two atoms to form $AB_2(g)$. If $A(a)$ is surrounded by three $B(a)$ atoms then a random choice is made to pick two of the three $B(a)$ atoms to form $AB_2(g)$, which desorbs leaving behind two vacant sites. (v) If on the other hand B_2 is adsorbed then the six nearest neighbours are scanned randomly for the presence of either an $A(a)$ atom or an $AB(a)$ molecule. In the first case an $AB(a)$ is formed, $B(a)$ vacates its site and moves to the site occupied by $A(a)$. In the second case an $AB(g)$ is formed, it desorbs leaving behind two empty sites. If all the NN sites are of the same kind then a random choice is made. If on the other hand it is surrounded by both then according to Albano the formation of $AB_2(g)$ has precedence over the formation of $AB(a)$.

With this simulation procedure the coverages of $A(a)$, $B(a)$ and $AB(a)$, (θ_A , θ_B and θ_{AB}) as a function of partial pressure p are plotted in figure 1 (shown as curves I). The data points are averages taken over 10 samples for $L = 40$. We obtain an IPT at $p = \frac{2}{3}$ in agreement with Albano's results. The single species coverage at $p = 0.0$ and for $p > \frac{2}{3}$ is also consistent with Albano's quoted values (i.e. 0.907). However, we find a consistently higher coverage for $A(a)$ and a consistently lower coverage for $AB(a)$ in the region $0 < p < \frac{2}{3}$. At about $p = 0.65$ this disagreement is roughly of the order of 20%. However, the sum $\theta_A + \theta_{AB}$ is roughly 0.9 in agreement with Albano's results. The coverages we obtained are more or less independent of the lattice size. We tried different lattice sizes starting from $L = 16$ and moving on to $L = 200$, with the same results.

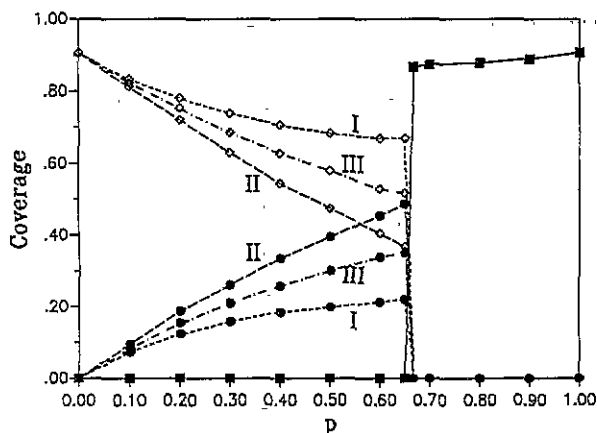


Figure 1. Plots of surface reactant coverages (θ_A , θ_B and θ_{AB}) versus p for the case when formation of $AB_2(g)$ has precedence over the formation of $AB(a)$ (curves I), equal probability for the formation of $AB(a)$ and $AB_2(g)$ (curves III) and $AB(a)$ has precedence over the formation of $AB_2(g)$ (curves II). \diamond — θ_A , \bullet — θ_{AB} , and \blacksquare — θ_B .

Obviously, the case when $B(a)$ is surrounded by $A(a)$ and $AB(a)$ and the formation of $AB_2(g)$ has precedence over that of $AB(a)$, according to our calculation, gives a different result than that presented by Albano. Let us denote this case as I (figure 1). There are two other possibilities: formation of $AB(a)$ has a precedence over $AB_2(g)$ (case II) and the two formations are equally probable (case III). With these two extra cases in model M1 we obtain the results as shown in figure 1 and marked as II and III respectively. All the

three cases (I, II and III) give the same IPT but the coverage rates θ_A and θ_B as function of p are different due to different formation precedence. We notice that θ_{AB} increases (as p increases) more rapidly in case II than in case III and even more rapidly than in case I (the situation considered by Albano). According to present work, the results quoted by Albano (figure 1 in his paper) are consistent when we assign equal probability of formation to $AB(a)$ and $AB_2(g)$.

We shall further add that besides the usual monomer-dimer (MD) reaction $CO + \frac{1}{2}O_2 \rightarrow CO_2$, since the work of Ziff *et al* [2], the same model has been applied to other MD reactions like $CO + NO \rightarrow CO_2 + \frac{1}{2}N_2$ which do not fall into the same class as CO-O₂ reaction [3]. In the case of DD reaction also there are a number of other possibilities, besides the one studied by Albano, which we are studying presently.

In conclusion, the coverages of $A(a)$ and $AB(A)$ for $0 < p < \frac{2}{3}$ are very sensitive to the criteria adopted for assigning to the formation of $AB(a)$ or $AB_2(g)$. The other models (in particular $M3$) in Albano's work should be further studied with different assigning criteria.

References

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