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Eley–Rideal model for a monomer–trimer catalytic reaction of the type $A + B_3 \rightarrow AB$: a Monte Carlo simulation study

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Abstract

The phase diagram of the monomer–trimer model has already been studied on the basis of (a thermal) Langmuir–Hinshelwood (LH) mechanism, the details of which can be found in the literature. Here, we have studied the effect of the Eley–Rideal (ER) mechanism on the phase diagram of this system. With the introduction of the ER process, the continuous transition of the LH model has been eliminated, while reactive window width and the production rate have been increased. The production rate can be represented by simple mathematical equations. The effect of monomer diffusion and desorption has also been studied for both models. Results are compared and some interesting observations are reported.

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1. Introduction

Knowledge of the details of catalytic reaction systems is in general of great chemical and industrial importance. The scientific interest in the study of these processes is due to the emergence of a rich and complex variety of physical chemistry phenomena including, e.g., critical phenomena and irreversible phase transitions, propagation and interference of chemical waves of adsorbed reactants, etc. The detailed understanding of such catalytic reactions is very important in applied research but rarely has such an understanding been achieved either from experiment or from theory. An investigation of the lattice models of catalytic surface reactions has been extremely helpful in gaining a better understanding of the kinetics of catalytic processes. Ziff, Gulari and Barshad (ZGB) [1] and Dumont *et al* [2] introduced a monomer–dimer (MD) model, which has been used to study a reaction system of the type $2A + B_2 \rightarrow 2AB$. This reaction mimics the catalytic oxidation of CO. This model is generally known as the ZGB model. Details of this seminal work can be found in the literature

elsewhere [3, 18]. Ever since this seminal work, a number of authors have modified this model to study different reaction systems of interest [3–21]. Meakin and Scalapino [3] investigated the effect of the lattice type on the reactive window of the ZGB model. They found that for a hexagonal lattice (each surface site has six nearest neighbours) the reactive window (the region between two phase transitions where continuous production of AB takes place) increases in size as compared to the usual square lattice. The second-order phase transition (y_1) occurs at $y_A = 0.360 \pm 0.005$ whereas the first-order phase transition (y_2) occurs at $y_A = 0.561 \pm 0.001$, where y_A represents the partial pressure of the monomer A.

The kinetics of an irreversible dimer–dimer surface reaction of the type $A_2 + B_2 \rightarrow 2AB$ with desorption of the dimer B_2 has been studied by Khan *et al* [4] on a square lattice. For the desorption probability (P) of B_2 equal to zero, a single discontinuous transition separating an A+ vacancies-saturated surface from a B+ vacancies-saturated surface is obtained at $y_B = 0.50$ (y_B is the feed concentration of the dimer B_2). With the increase in P a steady reactive state (SRS), which is separated from the poisoned state by two continuous transitions, is obtained for this system. The positions of the transition points depend upon the value of P . Kohler and Avraham have reported the results of a hypothetical dimer–trimer (DT) model of the type $3A_2 + 2B_3 \rightarrow 6AB$ on a hexagonal lattice [5]. They observed a phase diagram in which a SRS is separated from a B+ vacancies-poisoned state by a continuous transition (y_1) and from an A+ vacancies-poisoned state by a discontinuous transition (y_2). The phase diagram seems to resemble the standard ZGB model qualitatively with the difference that for $y_A < y_1$ ($> y_2$) in the ZGB model the surface is poisoned with 100% B (A). However, a number of discrepancies can be found in their paper [6]. Khan *et al* [6] have studied the same model on a square surface. A consequence of the work is that the lattice type has a significant effect on the reactive window of the system. The reactive window width of ≈ 0.12 (as shown by Kohler and Avraham for the hexagonal case) has been significantly reduced to ≈ 0.02 for the square lattice. Khan *et al* [6, 7] have also studied a hypothetical monomer–trimer model of the type $3A + B_3 \rightarrow 3AB$ on square and hexagonal surfaces. Their model is based on the Langmuir–Hinshelwood (LH) mechanism. The model reveals a phase diagram which is very similar to that of the ZGB model. For a square lattice, the values of y_1 and y_2 are 0.190 ± 0.005 and 0.465 ± 0.005 , respectively. By moving from a square to a hexagonal lattice, the general features of the phase diagram remain the same. The value of y_1 remains almost the same whereas the value of y_2 shifts from 0.465 to 0.525 ± 0.005 .

One class of catalysed reactions is imagined to proceed via the Eley–Rideal (ER) mechanism, in which a gas phase reactant, never in equilibrium with the surface, directly picks up a fragment of the adsorbed reactant and forms a product, which leaves the surface. This class of reaction, halfway between the gas phase type and LH type, is of interest in surface science. Jackson and Persson [8] have studied the dynamics of a ‘hot’ hydrogen dimer in the ER process (the direct reaction between a gas phase H atom and an adsorbed H atom) using a fully three-dimensional flat surface model for Cu(111). Meakin [9] explored the effects of the ER process on the simple ZGB model for the catalytic oxidation of CO by oxygen. The ER process results in the formation of a new regime in which a continuous reaction can be sustained. As soon as CO partial pressure departs from zero, continuous production of CO_2 starts. This production continues until $y_{CO} \approx 0.497$, where a first-order phase transition terminates this activity and the surface is poisoned by CO. Employing the ER process, he has also studied monomer–monomer reaction system and got similar results. Recently Khan and Ahmad [10] have used Monte Carlo simulation to explore the effects of the ER mechanism on a simple LH model for the NO–CO catalytic reaction on a square surface. The model generates a very small reactive window. The moment CO partial pressure departs from zero, continuous production of CO_2 and N_2 starts. A first-order transition terminates the catalytic

activity at $y_{CO} = 0.033$ and the surface is poisoned with a combination of CO and N. The introduction of diffusion of the species shifts the transition point from $y_{CO} = 0.033$ to higher values of y_{CO} . The introduction of desorption of CO in the model also increases the width of the reactive window.

The objective of this paper is to explore the possible effects of the ER process on the phase diagram of the LH type model for a hypothetical (superficial) ‘monomer–trimer’ surface catalytic reaction system. In this study, we shall also investigate the effect of diffusion and desorption of the monomer on the phase diagram of the system. In our LH model [6], we have ignored the diffusion and desorption of the monomer. However, for a comparative study with the ER model we shall also study the diffusion and desorption of the monomer in the LH model. The sole purpose of this study is to get theoretical knowledge of the behaviour of the species (monomer and trimer) on the surface so that more real but complicated monomer–trimer systems such as the water gas shift reaction may be studied with better understanding. The paper is structured as follows: in the following section the reaction model and the simulation procedure have been discussed. The results have been presented and discussed in section 3. Finally, the conclusions will be discussed in section 4.

2. Model and simulation

We have proposed the LH monomer–trimer (MT) model of the type $3A + B_3 \rightarrow 3AB$, which is symbolically represented by the following four equations:



With the introduction of the ER process, one has to add the following equation:



where S is an empty surface site, (g) refers to the gas phase and X^S represents the X adatom. There appears to be considerable uncertainty concerning the relative importance of the LH and ER reaction steps given by equations (3) and (4), respectively [9, 11]. It is worthwhile mentioning that the relative frequency of the LH reaction step and the ER reaction step depends upon trimer coverage. If the initial trimer coverage on the surface is higher (small y_A values), then the ER reaction step becomes dominant otherwise the LH reaction step becomes important [11]. We have investigated the addition of reaction step (4) to the usual simple LH model of the reaction system. Moreover we have also considered the effects of diffusion and desorption of the monomer A on the phase diagram of the model. The relative partial pressures of A and B_3 are y_A and $1 - y_A$, respectively. We have considered the square lattice of size $L = 128$ for this study. The four nearest neighbouring (nn) sites of a selected site S have been shown in figure 1. It has been observed that an increase in the lattice size changes the critical values slightly but the overall qualitative nature of the phase diagram remains the same [4, 13]. The periodic boundary conditions have been employed in order to avoid the surface effects.

The simulation starts with a clean surface. The only variable in our simulation is the feed concentration of A (y_A). The equilibrium coverages are measured as a function of y_A . In order to locate the critical points, ten independent runs each up to 50 000 Monte Carlo (MC) cycles are carried out. One MC cycle is equal to $L \times L$ trials. If all the ten runs proceed up to 50 000 MC cycles without the lattice getting poisoned, the particular point is considered to be within a SRS. The poisoning of even a single run is a sufficient criterion for considering the

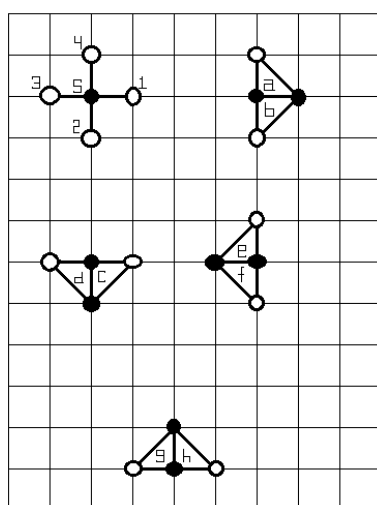


Figure 1. Four nearest neighbours of surface site S are marked as 1, 2, 3 and 4, respectively. Different possible choices of a trimer adsorption on a square lattice forming vertices of a right-angled triangle are shown by a, b, c, d, e, f, g and h, respectively (see text for detail). Solid circles represent adatoms whereas open circles represent the prospective sites for adsorption of other atoms of the trimer.

point to belong to the poisoned state. If the run does not end up in a poisoned state, then in order to get the coverages corresponding to the SRS, the initial 10 000 MC cycles are ignored (because the coverages show large variation in this regime) and the averages are taken over the subsequent 40 000 MC cycles (where the variation in the coverages is very small). The values of the coverages (production rate) are taken after every 10 MC cycles in the regime of 40 000 MC steps, so that the final coverage (production rate) is an average taken over 4000 configurations.

In the simulation of our model, a trial begins with the random collision of a gas molecule on a square lattice, which represents the surface. The colliding molecule is chosen to be $A(g)$ with a given probability y_A and $B_3(g)$ with probability $1 - y_A$. (a) If the impinging molecule is a trimer (B_3), the following cases happen: (i) a site S on the surface is randomly chosen. (ii) If the site is already occupied then the trial ends (the trimer backscatters from the surface) else two more adjacent vacant sites are also required in addition to the randomly selected site S since a trimer requires three sites to be adsorbed. These two sites are selected at random in such a way that the three sites constitute the vertices of a right-angled triangle as shown in figure 1. If the second picked site is marked as 4, then the two possible choices for forming vertices of a right-angled triangle are (4, 1, S) or (4, 3, S) as shown in figure 1. One of them is picked randomly. If all the randomly chosen sites are empty, then B_3 is adsorbed in atomic form on these sites (step 2). The adsorption of a trimer on triplets of linear vacancies is not allowed [9, 18] and there are two sets of the triplets of linear vacancies for a square lattice as shown by (1, S, 3) and (2, S, 4) in figure 1. (iii) After adsorption all three of the chemisorbed B^S adatoms scan their respective nn sites for A^S adatoms. The chemisorbed adatoms (A^S and B^S) sitting on adjacent sites form $AB(g)$ that desorbs from the surface leaving behind two vacant sites (step 3). (b) If the monomer $A(g)$ happens to be selected then there are two possibilities after the selection of a random site S: either the site is occupied or it is empty. If the randomly selected site is occupied by species other than a B adatom, the trial ends. If B^S occupies it, the reaction step (4) (i.e. Eley and Rideal step) takes place. In the case the randomly selected site

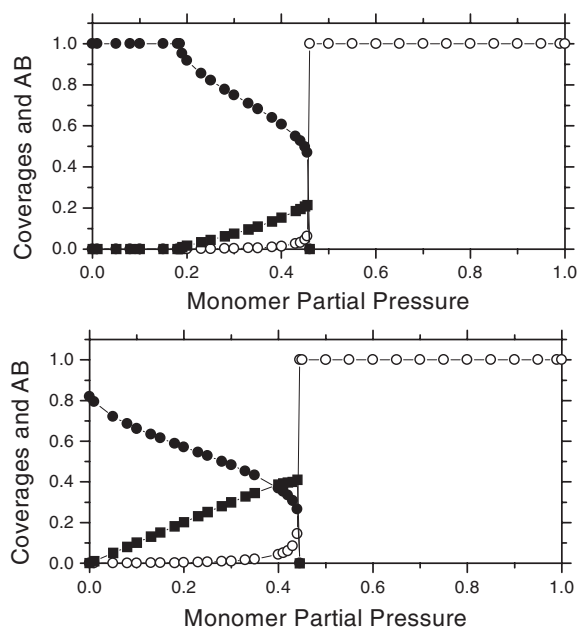


Figure 2. Coverages of trimers (solid circle), monomers (open circle) and production AB (solid square) as a function of monomer partial pressure for the LH model (top) whereas the same as above is also shown for the ER model (bottom). In both parts of the figure, diffusion and desorption of the monomer are ignored.

is vacant, then the monomer $A(g)$ adsorbs on it. After adsorption, all four nn sites are scanned randomly for B^S . If any of the four sites has a B^S , then the A adatom reacts with B^S forming $AB(g)$ that desorbs from the surface and the two sites are evacuated.

To incorporate the diffusion of A^S species in the aforementioned reaction scheme, we modify the simulation procedure slightly. If at the start of the trial the randomly selected site is empty or occupied by B^S , then the algorithm proceeds as mentioned earlier. However if the selected site is occupied by A^S , a nn site is selected at random. If the new site is occupied then the trial ends, otherwise it is allowed to diffuse to this site vacating the previous site. After a successful diffusion event, we investigate the nn sites for the presence of the reacting species (B^S). If B^S is found then it reacts with it according to step (3). It should be noted that diffusion of an A^S atom is introduced with a maximum probability equal to one.

In a similar way, a slight modification in the simulation procedure (step (b)) is made in order to incorporate desorption of the monomer. If the selected site is occupied by an A adatom then the possibility of its desorption is examined with the desorption probability d_m . In order to do this, a random number is generated and is compared with d_m . If it is less than d_m then the A^S adatom leaves the surface and the site is vacated, otherwise the trial ends. The rest of the simulation procedure is the same as discussed earlier.

3. Results and discussion

If the reaction step (4) is ignored then the results are well known [6]. Figure 2 (bottom) shows the situation when reaction step (4) is also considered along with the reaction step (3). For comparison purposes, a figure of the phase diagram has also been reproduced from [6], which is shown on the top of figure 2. In both cases, the coverages and the production rate are

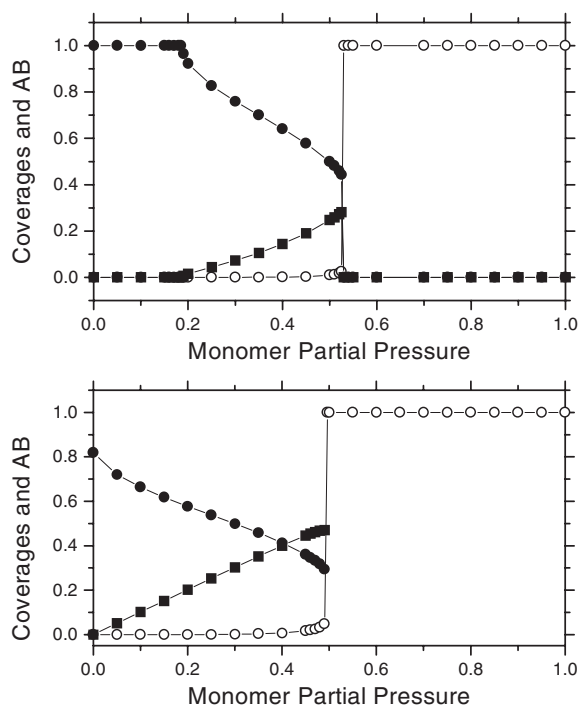


Figure 3. Same as in figure 2 when diffusion of the monomer is introduced in the LH and ER models.

plotted as a function of y_A . The LH model reveals a phase diagram very similar to that of the ZGB model with continuous (y_1) and discontinuous (y_2) phase transition points at 0.190 ± 0.005 and 0.460 ± 0.005 , respectively. However, in the ER model the continuous production of AB starts the moment monomer partial pressure departs from zero, which continues until $y_A = 0.450 \pm 0.005$, where a discontinuous phase transition (y_2) stops the catalytic activity. Figure 3 shows the phase diagrams of the system when the monomer diffusion is introduced in the LH (top) and ER (bottom) models. It can be seen that in the LH model the value of y_1 remains unchanged whereas the value of y_2 has been shifted to $y_A = 0.5250 \pm 0.005$, which is the same as that of the ZGB model for a square lattice. The production rate has also been increased with the introduction of diffusion. However, the qualitative behaviour of the coverages and the production rate are similar to that observed in figure 2 (top). A similar trend can also be seen in the ER model. With the diffusion of the monomer the value of y_1 is unchanged, whereas the value of y_2 is shifted to $y_A = 0.495 \pm 0.005$, which is the same as obtained by Meakin [9] in a similar study of the monomer–dimer reaction system on a square lattice. This means that the addition of diffusion in the LH monomer–trimer model gives a value of y_2 similar to the LH monomer–dimer model whereas the addition of diffusion in the ER monomer–trimer model gives values of y_1 and y_2 (and the window width) similar to the ER monomer–dimer model. It is observed that by introducing the reaction step (4) (without diffusion of the monomer) not only is the continuous transition eliminated but the product AB is also increased significantly. The value of y_2 , however, is almost the same in the two models. The production rate of AB becomes almost double with the inclusion of the reaction step (4). Figure 4 (top) shows mathematical fits of the data of the production rate (R) versus the monomer partial pressure (y_A). The best fits of the data (without diffusion of the monomer) are described

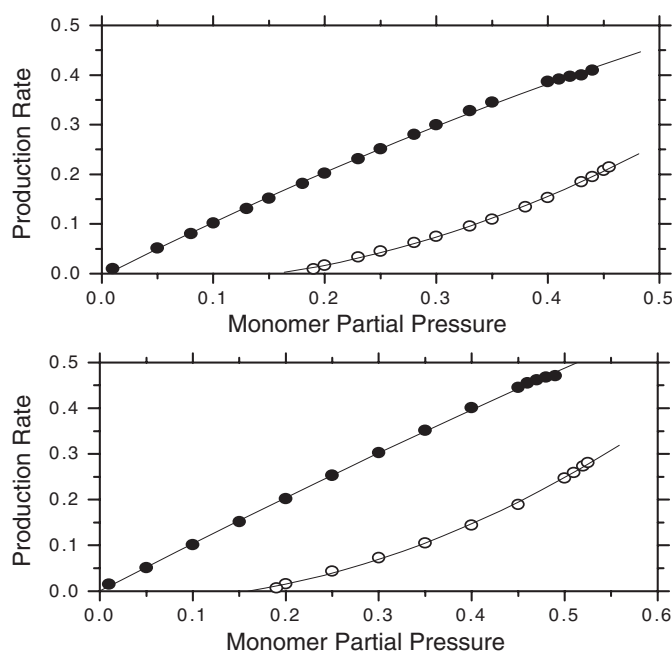


Figure 4. Production rates of the LH model (open circle) and the ER model (solid circle) as a function of monomer partial pressure when diffusion and desorption are ignored (top) and diffusion of the monomer is considered (bottom). The polynomial fits of the data are also shown. The details of the fit are in the text.

by $R = -0.0203 - 0.068 (y_A) + 1.27 (y_A)^2$ and $R = -0.006 + 1.125 (y_A) - 0.39 (y_A)^2$ in the LH and ER models, respectively. The standard deviations of the data are 0.0025 and 0.0035, respectively. However, when diffusion of the monomer is introduced, mathematical fits of the data of the production rate versus monomer partial pressure (y_A) are $R = -0.0212 - 0.056 (y_A) + 1.19 (y_A)^2$ and $R = 0.0003 + 1.05 (y_A) - 0.153 (y_A)^2$ in the LH and ER models, respectively, as shown in figure 4 (bottom). The standard deviations of the data are 0.0036 and 0.0037, respectively.

For low monomer (high trimer) partial pressure, the surface contains clusters of B atoms. In this region, reaction step (4) on one hand burns the chemisorbed B atoms of these clusters whereas on the other hand it creates isolated vacancies inside these clusters. On the isolated vacancies the monomer is easily chemisorbed, which triggers reaction step (3) too. In this way, the B atoms burn very quickly. The generation of isolated vacancies (due to ER reaction step (4)) precludes the adsorption of the trimers and therefore continuous transition is eliminated. The production starts the moment y_A departs from zero. Ultimately, we observe a situation as shown in figure 2 (bottom). In order to distinguish between reaction steps (3) and (4) in the catalytic oxidation of CO (monomer–dimer), experiments have been carried out with molecular beams impinging on the Pd surface [11, 21]. These experiments have shown that due to reaction step (4) the reactivity of CO is very fast in the region of highest coverage of the adsorbed oxygen (dimer). The LH reaction treatment is effective when (CO and O) surface coverages are low. These experimental observations are consistent with our findings in this monomer–trimer reaction system because in our model due to reaction step (4) the reactivity of the monomer is very fast in the region of highest coverage of the trimer. Our results are also consistent with the theoretical (Monte Carlo simulation) findings of Meakin [9] for the monomer–dimer reaction system. It follows from the above discussion that the role of

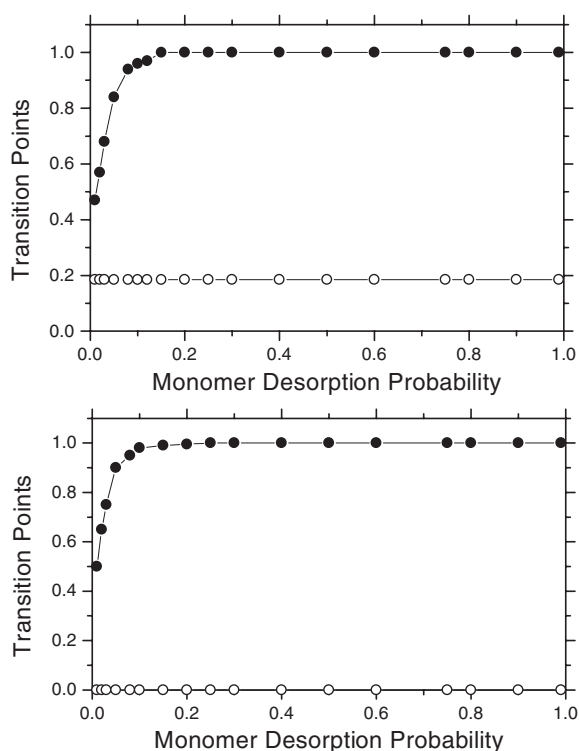


Figure 5. The values of transition points y_1 (open circle) and y_2 (solid circle) as a function of monomer desorption probability for the LH (top) and ER (bottom) models.

the ER process is the same in both monomer–dimer and monomer–trimer models because the ER process involves the direct interaction of the monomer (CO) with other reacting species. It implies that as far as the ER process is concerned the role of a monomer is more important as compared to the role of a dimer or a trimer in their respective reaction systems.

With the introduction of the probability of monomer desorption (d_m) in the two models, the situation significantly changes as shown in figure 5. In the LH model (top), with the increase in d_m the value of y_2 increases towards higher monomer partial pressure until $d_m = 0.14$ and thereafter it takes a fixed value. However, the value of y_1 remains constant. Figure 6 shows the phase diagram of the model when $d_m = 0.05$ (top) and 0.5 (bottom), respectively. For $d_m > 0.14$, a maximum window width is observed. The continuous production of AB starts the moment $y_A > 0.185$ and it continues until the supply of trimer is switched off. Even a very small amount of trimer is sufficient to sustain the catalytic activity. When $d_m < 0.14$, the production increases with y_A and goes to zero sharply at y_2 whereas for $d_m > 0.14$ (maximum window width) the production increases with y_A , attains a maximum value and thereafter decreases slowly to zero at y_2 . A similar behaviour is seen when the ER model is considered as shown in figure 5 (bottom). With the increase in d_m the value of y_2 increases towards the higher monomer partial pressure until $d_m = 0.20$ and thereafter it takes a fixed value. However, the value of y_1 remains constant. For $d_m > 0.20$, a maximum window width is observed. The continuous production of AB starts the moment $y_A > 0$ and it continues until the supply of trimer is switched off. When $d_m < 0.2$, the production increases with y_A and then goes to zero abruptly at y_2 whereas for $d_m > 0.2$ (maximum window width) the production increases with y_A , achieves a maximum value and thereafter decreases slowly to zero at y_2 . We plot the

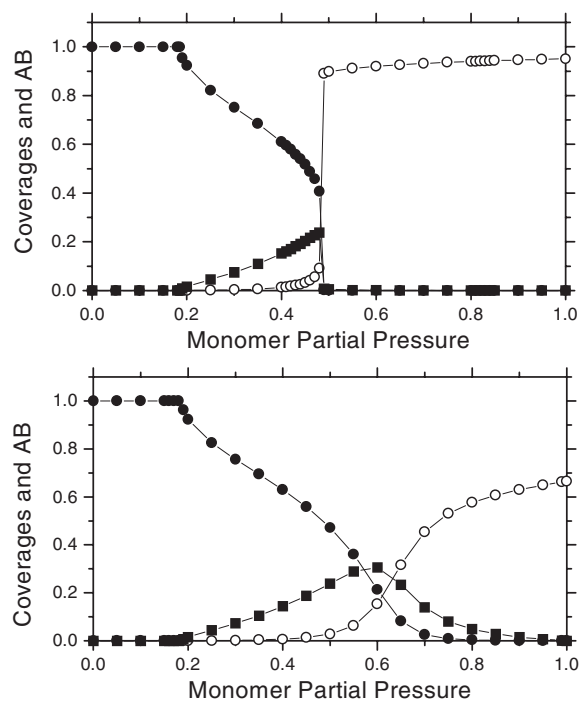


Figure 6. Coverages of trimers (solid circle), monomers (open circle) and production AB (solid square) as a function of monomer partial pressure for the LH model (without diffusion) when monomer desorption probabilities are 0.05 (top) and 0.50 (bottom), respectively.

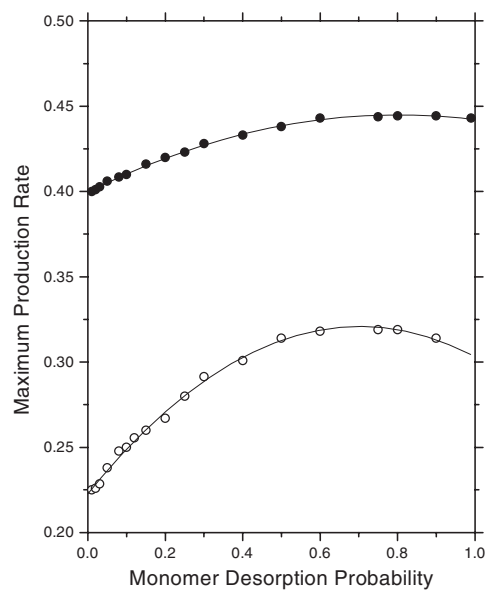


Figure 7. Maximum production rate as a function of monomer desorption probability for the LH (open circle) and the ER models (solid circle), respectively.

maximum production rate (R_{\max}) as a function of d_m (figure 7). The data are fitted through mathematical fits of the type: $R_{\max} = 0.223 + 0.279 (y_A) - 0.198(y_A)^2$ and $R_{\max} = 0.40 + 0.113 (y_A) - 0.071(y_A)^2$ for the LH and ER models, respectively. The standard deviations of the data are 0.0007 and 0.0023, respectively.

4. Conclusions

We have studied a hypothetical MT model on a square lattice. It is seen that the introduction of the ER process in the LH model changes the situation significantly. The continuous phase transition of the LH model is eliminated, the steady window width is widened and the production rate is enhanced significantly in our model. The productive activity starts the moment y_A departs from zero and a discontinuous point terminates the activity. The production rates can be represented in the form of simple mathematical equations. In a real experimental situation, the productive activity strongly depends upon temperature. In our simulations, the temperature is involved through desorption of the monomer and diffusion of the adatoms through the surface. It is observed that diffusion of the monomer does not change the qualitative nature of the situation of a particular model. However, the window width and the production rate of AB are increased in the two models. The value of y_2 is shifted towards higher values of y_A with the increase in d_m .

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