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Kinetic phase transitions in the A–B₂–D surface reaction model

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Abstract. A monomer–dimer–monomer (A–B₂–D) lattice surface reaction model is proposed, in which two adsorption parameters X_A and X_D are involved. The phase diagram for this model is determined by the partial simulation method. For the case of no desorption being considered, six phases are found, which are the two-species saturated phases S_{AD} , S_{BD} , S_{BE} and S_{AE} (E denotes the intermediate product AB), the one-species saturated phase S_B and the steady reactive phase R. The R and S_B phases are restricted to the line $X_A = X_D$. Phase transitions between two-species phases or between R and S_B are all second order, while that between R and S_{AD} is first order. It appears that there exists a pentacritical point at $X_A = X_D = 0.023 \pm 0.001$. If D* desorption is taken into account, the reactive phase R extends to a region of finite area.

1. Introduction

The kinetics of the catalytic surface reaction has been a topic of increasing interest in recent years, since the lattice model of the A–B₂ surface reaction was first introduced by Ziff, Gulari and Barshad (ZGB) [1]. Lattice models of surface reactions may take into account the microscopic fluctuations and correlations of the surface reactants, and so give further insight into the kinetics of surface reactions. Up to now, several types of the lattice model have been studied in the literature, among them the monomer–monomer (A–B) [2–5], the monomer–dimer (A–B₂ or A–BC) [1, 6, 7], the dimer–dimer (A₂–B₂ or AB–C₂) [8–10] and the dimer–trimer (A₂–B₃) [11] models are well known. All these models involve two reaction species and thus only one adsorption parameter; although simple they all show rich phase structures and interesting kinetics.

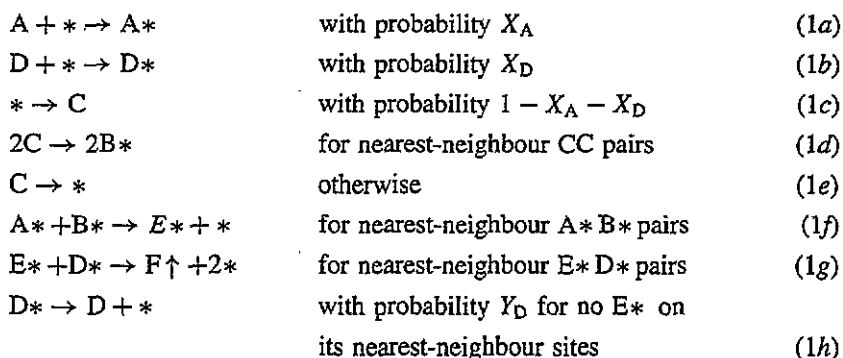
In this paper, we present an A–B₂–D surface reaction model which involves three reaction species: a dimer and two monomers. An adsorbed monomer A reacts with a half of an adsorbed dimer B₂ to form the intermediate product E, which in turn reacts with an adsorbed monomer D to form the final product F desorbing immediately. This reaction model mimics the oxidation of SO₂ on a catalytic surface (say MnO₂) in the presence of water vapour, which is important in environmental sciences, such as in studying the formation of acid mists or eliminating the SO₂ in exhaust. The phase diagrams for this reaction system are determined in the following two cases: (i) the desorption and diffusion of surface reactants are ignored, in this case our model is a direct generalization of the ZGB model [1] from two components to three; and (ii) the desorption process of adsorbed D*, which occurs in real reaction systems, is taken into account. In the latter case we focus on

the influence of D^* desorption on the steady reactive phase which is found to be in a linear region in the former case (see the text).

This paper is organized as follows. In section 2 a lattice model for the $A-B_2-D$ surface reaction is proposed, and the partial simulation (PS) method [12] is applied to this model. In section 3 simulation results are enumerated and discussed. Finally in section 4 a brief summary is given.

2. Model and simulation method

Similar to the cellular automaton (CA) version of the $A-B_2$ surface reaction model [13], in our $A-B_2-D$ model the catalytic surface is modelled as a square lattice, each site of which can be in one of the following six states: empty $*$, A-occupied A^* , B-occupied B^* , D-occupied D^* , E-occupied E^* and conditional occupied state C. All the lattice sites are updated simultaneously during one evolution step, according to the rules described below. The C state is necessary to describe the dissociative adsorption of a dimer B_2 ; conditional means that during the next evolution step a C state will become a B^* or $*$ state depending on whether there is a nearest-neighbour C state or not. A monomer $A(D)$ strikes the lattice with probability $X_A(X_D)$, and can be adsorbed by a $*$ (an empty state on the lattice becomes an $A^*(D^*)$ with probability $X_A(X_D)$); a dimer B_2 strikes the lattice with probability $X_B = 1 - X_A - X_D$ (an empty state becomes a C state with probability X_B), and can be adsorbed only by a nearest-neighbour empty pair (only a nearest-neighbour CC pair becomes a $2B^*$ state). If an A^* and a B^* are nearest neighbours, they react to form an E^* occupying one site with another site empty; if an E^* and a D^* are nearest neighbours, they react and desorb immediately leaving behind two empty states; however, if a D^* has no E^* on its nearest-neighbour sites, it desorbs with probability Y_D . We assume that the gas above the catalytic surface is continuously replenished to keep X_A and X_D constant, then the steps of the model can be summarized as follows.



where the upward arrow denotes the immediate desorption of the product F. Diffusion of surface reactants are not considered in this model.

To take into account the stoichiometry of two-site processes, it is required that each site belongs to only one nearest-neighbour pair at the most (this requirement was first considered by Ziff *et al* for a modified CA $A-B_2$ surface reaction model [14], where a nearest-neighbour pair that meets the stoichiometry requirement is called a 'matching' nearest-neighbour pair). We consider this requirement in the course of simulating where, for example, a D^* that has several nearest-neighbour E^* only reacts with one of them, and such cases as $B^*A^*B^* \rightarrow 2E^*$ or $CCC \rightarrow 3B^*$ or $4B^*$ etc are prohibited.

We use the PS method to obtain the phase diagrams of the above reaction model. In this method we only carry out simulations of the microscopic processes which are of significant importance, such as the processes of dimer adsorptions and two-site reactions; we treat other processes in a mean-field way. It had been shown that this method is very effective in investigating the phase diagram of the A-B₂ surface reaction [12]. Now we apply this method to the presented model.

Let N_0 , N_A , N_B , N_D , N_E and N_C represent, respectively, the numbers of *, A*, B*, D*, E* and C states on the lattice ($N_0 + N_A + N_B + N_D + N_E + N_C = N$, where N is the total number of lattice sites), and N_{AB} , N_{ED} and N_{CC} represent, respectively, the numbers of A*B*, E*D* and CC pairs that satisfy the stoichiometry requirement on the lattice. Then from (1a)-(1h) one can write the relations between those numbers at time t and $t + 1$ as follows.

$$N'_0 = 2N_{ED} + N_{AB} + N_C - 2N_{CC} + (N_D - N_{ED})Y_D \quad (2a)$$

$$N'_A = N_A + N_0X_A - N_{AB} \quad (2b)$$

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

$$N'_C = N_0(1 - X_A - X_D) \quad (2d)$$

$$N'_D = N_D + N_0X_D - N_{ED} - (N_D - N_{ED})Y_D \quad (2e)$$

$$N'_E = N_E + N_{AB} - N_{ED} \quad (2f)$$

where the quantities with a prime refer to the time $t + 1$, and the term $(N_D - N_{ED})Y_D$ represents the contribution from D* desorption. Note that these equations represent the changes of occupation numbers in one time step, i.e. a time interval in which all lattice sites are updated simultaneously.

The numbers N_{AB} , N_{ED} and N_{CC} are related to the local correlations of surface reactants, they may be obtained by carrying out 'trials' or simulations of the two-site processes. To obtain N_{CC} , for example, one may 'place' N_C C states randomly on the lattice, and then count the number of nearest-neighbour CC pairs. Similarly, to obtain N_{AB} , one places N_A A*s and N_B B*s randomly on the lattice and counts the number of nearest-neighbour A*B* pairs. In these trials the distributions of species on the lattice are simplified to the one-site approximation.

We perform the simulations as follows. The positions of all lattice sites are labelled by integer numbers from 0 to $N - 1$. At each time step when N_A , N_B , N_E , N_D and N_C are found from (2a)-(2f), a 'random number generator' generates N_A , N_B , N_E , N_D and N_C random integer numbers on $[0, N - 1]$ respectively, the positions of A*, B*, E*, D* and C states on the lattice are modelled as these five random integer number sequences. Then N_{AB} , N_{ED} and N_{CC} are calculated with a computer.

As described above, in the PS method one looks at the surface reaction in a number space: the square lattice (together with periodic boundary conditions) only means that each site has four nearest-neighbour sites, and updating the lattice means only changing the set of occupation numbers. Thus the PS method is essentially a mean-field method, supplemented with computer simulations. With this method, one may obtain qualitatively reliable results for phase diagrams of surface reaction systems [12] with much less work.

3. Results and discussions

Simulations have been carried out on an $N = 64 \times 64$ lattice with periodic boundary conditions and initial values: $N_0 = N$, and $N_A = N_B = N_C = N_D = N_E = 0$. The average coverage fractions $\theta_A = N_A/N$, $\theta_B = N_B/N$, $\theta_D = N_D/N$ and $\theta_E = N_E/N$ are obtained

when the system has reached a steady state. Usually, 10^2 – 10^4 time steps are needed to reach such a state.

3.1. Case I: no desorption ($Y_D = 0$)

For the case with no desorption six different phases are found from the simulations (figure 1(a)): the two-species saturated phases with A* and E* (S_{AE}), A* and D* (S_{AD}), B* and D* (S_{BD}) and B* and E* (S_{BE}); the one-species saturated phase with B* (S_B) and the reactive phase (R). The phase S_{BD} lies in the region with relatively small X_A , while the S_{AE} and S_{BE} lie in the region with relatively small X_D . Figure 1(b) is an amplified diagram for $X_B > 0.6$.

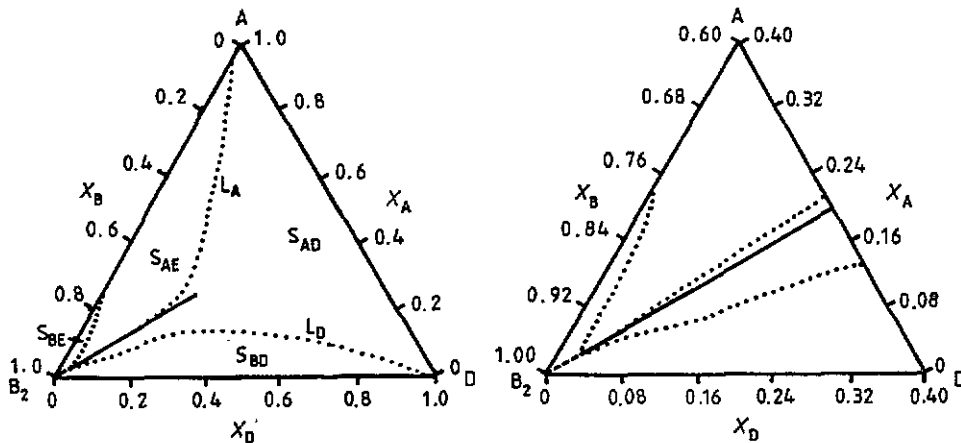


Figure 1. (a) Phase diagram for $Y_D = 0$. Dotted lines denote the second-order transition lines between two-species saturated phases, the one-species saturated S_B and the steady reactive phase R are represented by broken and full lines respectively. A pentacritical point seems to exist, as shown in (b). The probabilities corresponding to a given point inside the triangle may be read along the X_A , X_D and X_B axes.

Some remarks on the phase diagrams can be made.

(i) The two-species saturated phases are separated by four critical lines labelled by L_A , L_B , L_D or L_E (the phases S_{AE} and S_{AD} are separated by L_A , S_{AD} and S_{BD} by L_D , S_{BD} and S_{BE} by L_B , and S_{BE} and S_{AE} by L_E). On the critical line L_i the corresponding coverage θ_i has its maximum value $\theta_i \approx 1$ ($i = A, B, D$ or E), departing from this line θ_i decreases continuously while another coverage θ_j increases correspondingly, forming a saturated phase S_{ij} . This suggests that the transitions across these lines are second order. The variations in coverage across these lines are illustrated in figure 2.

Figure 2(a) shows that coverages θ_A , θ_D , θ_E vary as a function of X_D (X_A is fixed on 0.4) and at the point $X_D = X_{D1}^C = 0.1667 \pm 0.0001$, the system changes from the phase S_{AE} ($X_D < X_{D1}^C$) to the S_{AD} ($X_D > X_{D1}^C$). Similarly, in (b) and (c) corresponding transitions occur at $X_D = X_{D2}^C = 0.0166 \pm 0.0001$ (X_A is fixed at 0.15) and $X_A = X_{A1}^C = 0.1491 \pm 0.0001$ (X_D is fixed at 0.4) respectively; while in (d) for a fixed value $X_D = 0.02$, a transition occurs at $X_A = X_{A2}^C = 0.02$ which is determined precisely, in contrast to (a), (b) and (c) where the transition points are only approximately located. This simulation result suggests that the coverage θ_B may really reach its maximum value on the line L_B and form a saturated phase S_B .

Indeed, to reach S_B ($\theta_B = 1$ and $\theta_A = \theta_E = \theta_D = 0$) it is necessary that by the

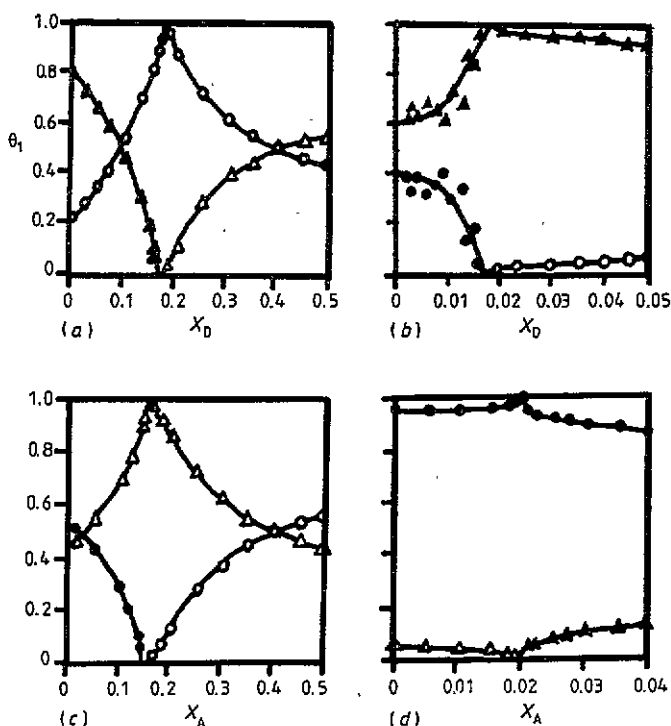


Figure 2. Variations in the coverages θ_A (○), θ_B (●), θ_D (△) and θ_E (▲) across the lines L_A ((a)), L_E ((b)), L_D ((c)) and L_B ((d)).

end of the process all created A*s (the summation of A*s created in all time steps) have been transformed into E*s and all created D*s and E*s have been annihilated, through the reactions of A* with B* and E* with D*. Note that for correct stoichiometry one A* transforms one E* and one D*(E*) reacts with one E* (D*). Thus it is necessary for all created A*s to be equal to the number of all created D*s. For a sufficiently large system this requirement may be easily satisfied on the line $X_A = X_D$, since the adsorption of the two monomers A and D is equivalent on this line; whereas there is no equivalency in the adsorption between a dimer B₂ and a monomer A (or D) to support the existence of S_A, S_E and S_D.

(ii) The phases R and S_B lie on the line $X_A = X_D$, S_B is located in the range $0 < X < X_1 = 0.023 \pm 0.001$ (the broken line in figure 1), and R is in the range $X_1 < X < X_2 = 0.251 \pm 0.001$ (the full line), where $X = X_A = X_D$. Departing from this line the system drops to two-species saturated phases, in either a continuous way (for $0 < X < X_1$, see figure 2(d)) or a discontinuous way (for $X_1 < X < X_2$). Along this line the coverages θ_A , θ_B , θ_D and θ_E vary with X continuously at the critical point X_1 but discontinuously at the critical point X_2 , suggesting that X_1 is a second-order phase transition point while X_2 is a first-order one. In figure 3 we present the variations in coverage with X, which exhibit an A-B₂-like phase structure as presented in [1].

(iii) As shown in figure 1, in our simulations it is found that the five lines R, L_A, L_B, L_E and L_D appear to converge at the point $X_A = X_D \approx 0.023$. The lower part of the critical line L_A is too close to the reactive line R to be seen clearly in figure 1(a); however, we have examined these two lines carefully and found that they are still distinguishable near

the point $X_A = X_D = 0.05$ (figure 1(b)). Hence a reasonable conclusion is that the point $X_A = X_D \approx 0.023$ is a pentacritical point. Further examinations of this conclusion are difficult in our simulations because the processes proceed extremely slowly and fluctuations play an increasingly important role as this critical point is approached.

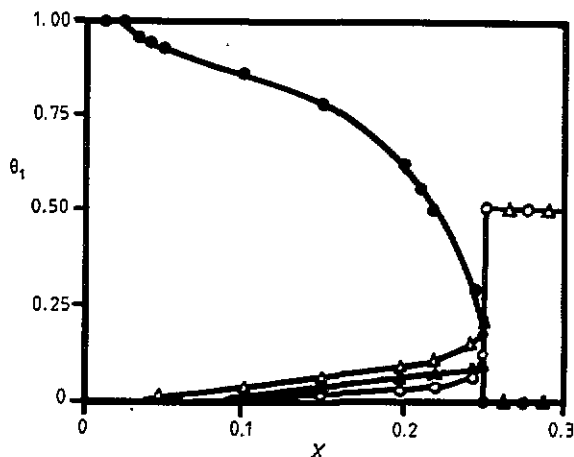


Figure 3. Phase transitions along the line $X_A = X_D$. Coverages of A(O), B(●), D(Δ) and E(\blacktriangle) as a function of X ($X = X_A = X_D$). Transitions occur at two points $X_1 = 0.023 \pm 0.001$ (second order) and $X_2 = 0.251 \pm 0.001$ (first order).

(iv) Finally, we would like to give some simple analyses of the phase diagram of the A-B₂-D model. Clearly the occurrence of the two-species saturated phases S_{AB} and S_{DE} are prohibited by the reactions of A* with B* and D* with E*; however, if one of the coverages θ_A , θ_B , and θ_D first decreases to zero before the reaction system reaches a steady state, the system will tend to one of the four two-species saturated phases: S_{AE} , S_{AD} , S_{BD} and S_{BE} . If the first coverage to vanish is θ_D (usually for small X_D), the system will eventually tend to S_{AB} or S_{BE} , depending on the next coverage to vanish being θ_B or θ_A . Similarly, if the first coverage to vanish is θ_A , the system will eventually tend to S_{BD} or S_{BE} , while if the first coverage to vanish is θ_B , the system will tend to S_{AD} or S_{AE} . The reaction condition $X_A = X_D$ may be verified by a mean-field analysis: defining the average coverage of ij pairs as $\theta_{ij} = 2N_{ij}/N$ one may easily write the following rate equations from (2b), (2e) and (2f):

$$d\theta_A/dt = \theta_0 X_A - \frac{1}{2}\theta_{AB} \quad (3a)$$

$$d\theta_D/dt = \theta_0 X_D - \frac{1}{2}\theta_{ED} \quad (3b)$$

$$d\theta_E/dt = \frac{1}{2}\theta_{AB} - \frac{1}{2}\theta_{ED} \quad (3c)$$

When the reaction system reaches a steady state, i.e. $d\theta_i/dt = 0$ ($i = 0, A, B, C, D$ and E), the above equations give two solutions: one solution is $X_A = X_D$, which corresponds to the reactive state in the case $\theta_0 \neq 0$, and another is $\theta_0 = 0$, $\theta_{AB} = 0$ and $\theta_{ED} = 0$, which corresponds to the saturated states. One may also write similar rate equations corresponding to (2a), (2c) and (2d) which are useful in determining the reactive range on the line $X_A = X_D$, but for a preliminary verification of the occurrence of reactive and saturated phases, only equations (3a), (3b) and (3c) are needed.

3.2. Case II: D* desorption ($Y_D \neq 0$)

First we consider the case $Y_D = 1$, i.e. an adsorbed D* without any nearest-neighbour E* will promptly desorb. The phase diagram is shown in figure 4. Comparing this diagram with that in figure 1(a), significant changes are found.

The phases S_{BD} and S_B now disappear; the phase S_{AD} reduces to a one-species saturated phase S_A ; while phases S_{AE} , S_{BE} and R extend considerably towards the region with large X_D . All these changes are reasonable, since no adsorbed D* can be retained on the lattice for more than one time step. Again, transitions between saturated phases S_A and S_{AE} , and S_{AE} and S_{BE} , are second order; while that between R and all saturated phases is first order. Two points $X_A = X_D = 0.031 \pm 0.001$ and $X_A = X_D = 0.223 \pm 0.001$ are found to be tricritical points.

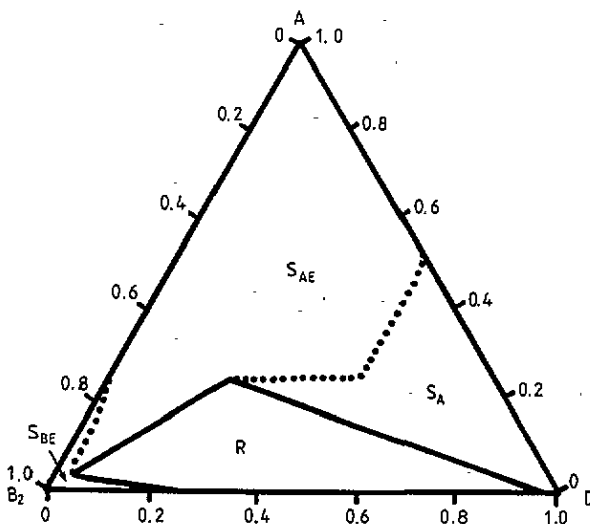


Figure 4. Phase diagram for $Y_D = 1$.

Now let us focus on the changes in the steady reactive region with desorption probability Y_D . Further simulations indicate that, as Y_D decreases, the region of R gradually reduces, mainly due to the lowering in the right-hand boundary line of R phase (figure 5); in contrast to this, the left-hand bound is hardly affected by Y_D , while changes in the low bound make a negligible contribution to the changes of the R region.

In figure 6, we present variations in the right-hand bound of R (X_D^C) with Y_D for a fixed $X_A = 0.1$, on a log-log scale. For small Y_D (say $Y_D < 0.1$), the variation of X_D^C with Y_D may be described by a power relation:

$$X_D^C \sim Y_D^\beta$$

where the exponent β has a value 0.39 ± 0.02 .

4. Summary

For the A-B₂-D model in the case in which no desorption is considered (Case I), the surface reaction system has six phases: the two-species saturated phases S_{AE} , S_{AD} , S_{BD} and S_{BE} , the one-species saturated phase S_B and the reactive phase R. The phases R and S_B lie on

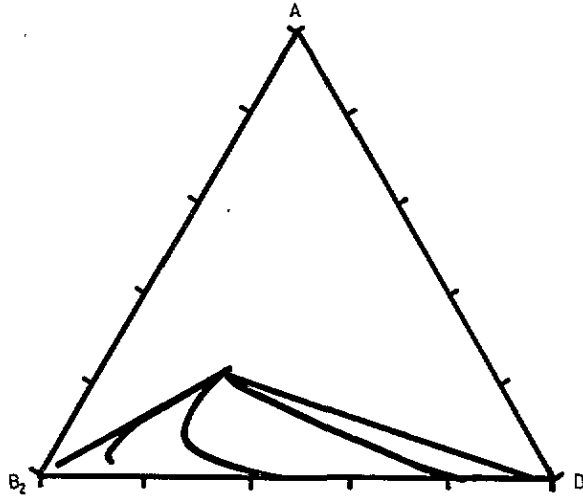


Figure 5. The right-hand bound of R as a function of Y_D . The five lines correspond, from left to right, to $Y_D = 0, 0.001, 0.01, 0.1$ and 1 respectively.

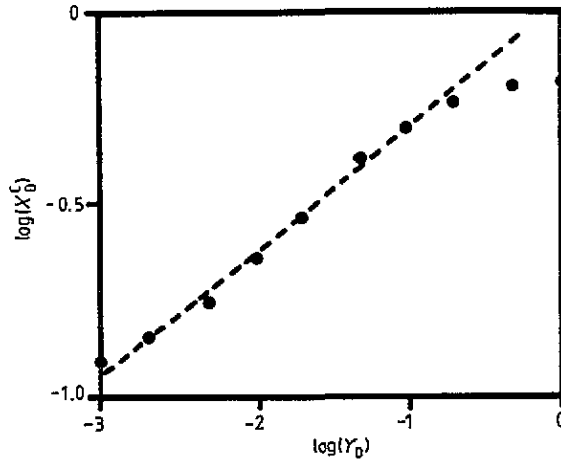


Figure 6. The variation in X_D^C with Y_D for a fixed $X_A = 0.1$, plotted on a log-log scale.

the line $X_A = X_D$. Transitions between the two-species saturated phases or between R and S_B phase are all second order, while that between R and S_{AD} is first order. It seems that there exists a pentacritical point located at $X_A = X_D = 0.023 \pm 0.001$.

The presented model mimics the catalytic surface reaction: $\text{SO}_2 + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$, in which water is in the vapour state. It is shown experimentally that under normal conditions no appreciable desorptions of $\text{SO}_2(\text{A})$ and $\text{O}_2(\text{B}_2)$ are observed [15], thus we only consider the desorption of $\text{H}_2\text{O}(\text{D})$ in the model. Simulation results indicate that when D^* desorption is taken into account (Case II), even for a desorption probability as small as $Y_D = 0.001$, the reactive phase is no longer indicated on a line, but in a region with finite extension.

Acknowledgments

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