Oscillatory kinetics of reactions on solid surfaces resulting from bistability and diffusion limitations

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Considering as an example the $2A + B_2 \rightarrow 2AB$ reaction occurring on the surface of a spherical catalyst, we demonstrate that heterogeneous reactions may exhibit oscillatory behavior at *isothermal* conditions if the bistability of the nonoscillatory surface kinetics is combined with diffusion limitations in the gas phase.

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Oscillatory chemical reactions have been the subject of many experimental and theoretical studies over the past 30 years. The most famous example is the Belousov-Zhabotinskii reaction [1] occurring in the liquid phase and exhibiting spectacular spatiotemporal color variations. More recently, the interest has been focused on heterogeneous catalytic reactions [2,3] [an already classical example, reported first by Ertl and co-workers [4], is CO oxidation on Pt(001)]. In both cases, the oscillatory behavior is due to nonlinear coupling between different elementary processes.

The bulk of the systematic studies of oscillations in heterogeneous reactions have concerned systems where all the important processes are occurring on a solid surface [the physical factors behind oscillations are believed to be (i) a coverage dependence of the activation energies for reaction steps, (ii) empty-site requirement for the reaction, (iii) buffer steps, (iv) oxide formation, or (v) surface reconstruction [2,3]]. The gas-phase concentrations are then constant or correspond to the conditions of the so-called well-stirred reactor [3]. A few recent studies [5] analyze the global coupling between surface kinetics exhibiting oscillations and mass transport in the gas phase (the equations, employed to describe the coupling, are of the same type as those used for the well-stirred reactor). In the present paper, we address the question if oscillatory kinetics, under *isothermal* conditions, can be produced through the global coupling of surface kinetics and diffusion limitations in the gas phase for the case when the surface kinetics alone *cannot* produce oscillations. According to the literature (e.g., Ref. [3(a)], p. 125), "there is hardly any reason to believe that diffusional resistances are causative factors of the oscillations themselves." On the other hand, a combination of the kinetic bistability and mass-transport limitations in the well-stirred reactor is known to be able to cause oscillations [2,3]. Mathematically, the diffusion limitations near a catalyst and the mass-transport limitations in a well-stirred reactor are described quite differently (by partial and ordinary differential equations, respectively). Physically, however, the feedback resulting from diffusion limitations is qualitatively similar to that taking place in the well-stirred reactor. Thus, in analogy with the well-stirred reactor, one can expect that a combination of the kinetic bistability and diffusion limitations may induce oscillations. In this communication, we show that such oscillations are indeed possible, even when the diffusion limitation is restricted to only one reactant.

As an example, we consider the $2A + B_2 \rightarrow 2AB$ reaction on the surface of a spherical catalyst pellet. The reaction mechanism is assumed to be basically the same as for CO (or hydrogen) oxidation on Pt. It involves reversible monomolecular A adsorption, irreversible dissociative B_2 adsorption, and $A + B$ reaction between adsorbed species to form product AB molecules which desorb rapidly. The corresponding mean-field kinetic equations for the adsorbate coverages are as follows:

$$d\theta_A / dt = k_1 P_A (1 - \theta_A) - k_2 \theta_A - k_3 \theta_A \theta_B, \tag{1}$$

$$d\theta_B / dt = k_4 P_{B_2} (1 - \theta_A - \theta_B)^2 - k_3 \theta_A \theta_B, \tag{2}$$

where P_A and P_B are the reactant pressures, and k_1, k_2, k_3, and k_4 the rate constants for elementary steps. Equation (2) describes that preadsorbed A particles inhibit dissociative adsorption of B_2 molecules (through the second order term). On the other hand, no such site-blocking effect is exerted by adsorbed B particles for incoming A molecules [no θ_B in the parentheses of Eq. (1)].

Elementary steps of surface reactions exhibiting oscillations are usually fast. With reasonable values of the rate constants (Table I), the typical reaction rate is about 10^5 monolayers per second (ML/s) (in the absence of mass-transfer limitations). To describe oscillations under such conditions, we need in fact only the steady-state solutions to Eqs. (1) and (2) (the steady-state approximation for rapid steps is common in the theory of chemical oscillations [1]). The most interesting property of these solutions is bistability (Fig. 1). For a given pressure P_A, the steady state is unique at sufficiently low and high pressures P_{B_2}, respectively. At medium B_2 pressures, $P_{B_2}^0 \leqslant P_{B_2} \leqslant P_{B_2}^1$, Eqs. (1) and (2) have three solutions, of which the intermediate one (with respect to absolute coverage) is unstable and the other two are stable. At $T = 500$ K and $P_A = 1$ bar (Fig. 1), the critical B_2 pressures are $P_{B_2}^0 = 0.11$ bar and $P_{B_2}^1 = 0.29$ bar.

The term "stable" in the paragraph above corresponds to the mean-field approximation which does not take into account fluctuations of adsorbate coverages due to surface diffusion (as discussed in Refs. [6,7]). In our analysis, the "stable" nonunique solutions are considered to be really stable during the period of oscillations. This assumption is correct if the rate of formation of critical nuclei in the ad-

TABLE I. Input data for simulations of oscillatory kinetics of the $2A + B_2 \rightarrow 2AB$ reaction: $\mathscr{K}$ are the rate constants for the reactant fluxes, s the sticking coefficients, ν the preexponential factors, and E the activation energies. Note that the activation energy for A desorption rapidly decreases with increasing θ_A (this point is essential in order to reproduce realistic bistable kinetics at atmospheric pressures [9]).

Pellet radius: $R = 1$ cm
Number of active sites: $N_0 = 10^{14}$ cm^{-2}
Reaction conditions: $T = 500$ K,
$P_A = 1$ bar, $P_{B_2} = 0.5$ bar
Gas-phase diffusion coefficients:
$D_A \gg 0.1$ cm^2 s^{-1}, $D_{B_2} = 0.5$ cm^2 s^{-1}
A adsorption: $k_1 = s_A \mathscr{K}_A$
$\mathscr{K}_A = 10^8$ s^{-1} bar^{-1}, $s_A = 0.001$
B_2 adsorption: $k_4 = s_{B_2} \mathscr{K}_{B_2}$
$\mathscr{K}_{B_2} = 10^8$ s^{-1} bar^{-1}, $s_{B_2} = 0.01$
A desorption: k_2
$\nu_A = 10^{16}$ s^{-1}, $E_A = 35 - 10\theta_A$ kcal/mol
$A + B$ reaction: k_3
$\nu_r = 10^{13}$ s^{-1}, $E_r = 12$ kcal/mol

sorbed overlayer is low. The best argument in favor of stability of the mean-field solutions is that bistable kinetics are really observed experimentally [7] (for some additional arguments, see Ref. [8]).

To describe mass transfer in the course of reaction, we need to solve the time-dependent three-dimensional (3D) diffusion equations (with spherical symmetry) for the gas-phase concentrations $n_A(r,t)$ and $n_{B_2}(r,t)$ with the following boundary conditions at $r = R$ (R is the pellet radius):

$$D_A \frac{\partial n_A}{\partial r} = W, \quad D_{B_2} \frac{\partial n_{B_2}}{\partial r} = W/2,$$

where D_A and D_{B_2} are the diffusion coefficients, and $W(t)$ is the reaction rate (the number of AB molecules produced per unit area per second) calculated by employing the steady-state approximation for Eqs. (1) and (2) with *local* A and B_2 pressures.

To elucidate the evolution of the gas-phase concentrations, we recall that the steady-state solution to the 3D diffusion equation,

$$n(r) = n(R) + [n^* - n(R)](r - R)/r,$$

yields the following expression for the diffusion flux near the surface:

$$J = D[n^* - n(R)]/R, \tag{3}$$

where n^* is the concentration at $R \rightarrow \infty$. The maximum flux, $J_{max} = Dn^*/R$, corresponds to $n(R) = 0$. Comparing J_{max} and W, one can judge if the diffusion limitations are important or not.

In our simulations, diffusion limitations are assumed only for one reactant (for B_2 molecules). Diffusion of A molecules is considered to be rapid ($D_A n_A^*/R \gg W$), and no A concentration gradients are consequently established. In this
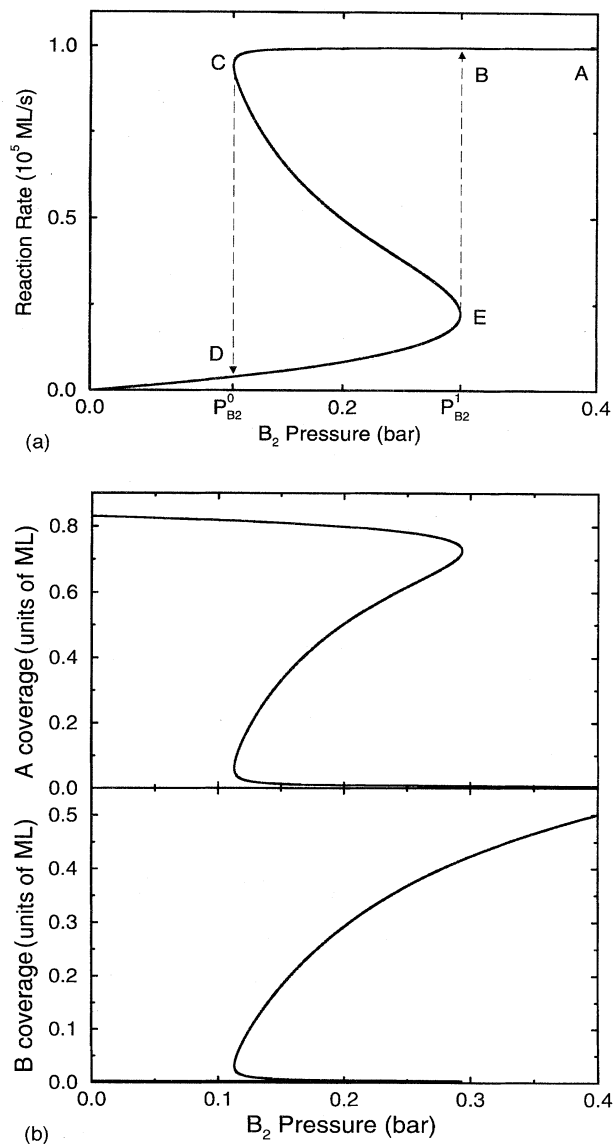

(a)

(b)

FIG. 1. (a) Reaction rate and (b) surface coverages as a function of B_2 pressure for $P_A = 1$ bar [according to the steady-state solution of Eqs. (1) and (2) with the rate constants presented in Table I]. Lines CD and EB in panel (a) correspond to the stepwise changes in the reaction rate in the course of oscillations (cf. Fig. 2).

case, the necessary conditions for generation of oscillations can be obtained by analyzing Fig. 1(a) in combination with Eq. (3) for B_2 molecules. First, we note that the B_2 pressure far from the surface should be larger than $P_{B_2}^1$. The latter makes it possible (through gradients in n_{B_2}) to reach all the bistable points and to create oscillations, provided that the kinetic parameters are of suitable magnitude. For example, let us consider that the B_2 pressure in the reactant mixture corresponds to the point A in Fig. 1(a) and that in the initial moment there are no concentration gradients (i.e., the local B_2 pressure is the same as in the reactant mixture). In this situation, the reaction rate is high (about 10^5 ML/s), i.e., the system is in the high-reactive state. With increasing time, the

local B_2 pressure will decrease due to rapid consumption and limited transport of B_2. Thus, the system will move to the left along the line AC [Fig. 1(a)]. In order to produce oscillations, we need to reach the point C, where a kinetic phase transition will occur to D, i.e., to the low-reactive state. Physically, this means that the diffusion limitations on the line AC must be so strong that the steady-state diffusion flux is not able to maintain the high-reactive state. Mathematically, this requirement is expressed as

$$D_{B_2}(n_{B_2}^* - n_{B_2}^0)/R < W_{max}/2, \qquad (4)$$

where $n_{B_2}^*$ and $n_{B_2}^0$ are the concentrations corresponding to pressures P_{B_2} and $P_{B_2}^0$, and W_{max} is the reaction rate in the high-reactive state (this rate is in fact constant along the line AC and we do not need to refer to the point where it is calculated). The left-hand part of Eq. (4) yields the steady-state diffusion flux provided that the pressure near the surface equals $P_{B_2}^0$ [cf. Eq. (3)]. The right-hand part is the rate of consumption of B_2 (the factor 2 takes into account the reaction stoichiometry).

If the system reaches point C, the reactive state becomes kinetically unstable, and we will have a very rapid transition from point C to point D (in the steady-state approximation, this transition is regarded as instantaneous) and the system will then be in the low-reactive state. Here, the consumption of B_2 is much less and the local B_2 concentration will recover. The system then starts to move along the line DE immediately after the kinetic phase transition $C \to D$ and will eventually reach the point E. The condition for this path is that the diffusion limitations of B_2 are not too severe, i.e.,

$$D_{B_2}(n_{B_2}^* - n_{B_2}^1)/R > W_E/2, \qquad (5)$$

where W_E is the reaction rate corresponding to the point E. If this condition is met, all the points on the line DE are unstable with respect to gas-phase diffusion and the system does reach the point E. Then, we will have a very rapid transition from E to B, i.e., the system will again be in the high-reactive state and will proceed along $B \to C$. Consequently, we have reached a state of repeated oscillations along $B \to C \to D \to E \to B$.

To elucidate in more detail the phenomenon described, it is instructive to construct an analytical solution to the problem under consideration and to estimate the period of oscillations. The latter is possible provided that the reaction rate in the high-reactive state is much higher than in the low-reactive state and also much higher than the average diffusion flux toward the surface (in this case, the reactive period becomes short compared to the unreactive one).

Let us first consider the evolution of the system along the line BC. Just after the transition from E to B, the B_2 concentration near the surface equals $n_{B_2}^1$ and the concentration gradients are relatively weak (because the reaction rate during the low-reactive period along $D \to E$ was low). For the motion along $B \to C$, the reaction rate is high and accordingly the B_2 concentration will rapidly decrease near the surface. The size of this B_2-depleted region is low compared to the pellet radius. The latter makes it possible to use the 1D diffusion equation to describe the high-reactive period of os-

cillations. An additional point simplifying the analysis is that the reaction rate is nearly constant during the high-reactive period, i.e., $W \simeq W_{max}$ along $B \to C$. In this case, the relevant solution to the 1D diffusion equation is given by

$$n_{B_2}(x,t) = n_{B_2}^1 - W_{max} \int_0^t G(x,t-t')dt', \qquad (6)$$

where x and t are the space and time coordinates ($x=0$ corresponds to the surface, and $t=0$ refers to the beginning of the active period), and

$$G(x,t) = (4\pi D_{B_2}t)^{-1/2}\exp(-x^2/4D_{B_2}t)$$

is the Green function. Near the surface, Eq. (6) yields

$$n_{B_2}(0,t) = n_{B_2}^1 - W_{max}(t/\pi D_{B_2})^{1/2}. \qquad (7)$$

Employing this equation and that $n_{B_2}(0,t) = n_{B_2}^0$ at the end of the reactive period, we obtain for the duration of this period

$$\tau_+ = \pi D_{B_2}(\Delta n/W_{max})^2, \qquad (8)$$

where $\Delta n = n_{B_2}^1 - n_{B_2}^0$.

The length of the low-reactive period, τ_-, can be calculated from the balance equation for the mass transfer

$$W_{max}\tau_+ + W_{low}\tau_- = 2\langle J_{B_2} \rangle(\tau_+ + \tau_-), \qquad (9)$$

where $W_{low} \simeq (W_D + W_E)/2$ is the average reaction rate during the low-reactive period (W_D and W_E are the reaction rates at the points D and E, respectively), $\langle J_{B_2} \rangle = D_{B_2}[n_{B_2}^* - \langle n_{B_2}(R) \rangle]/R$ the average diffusion flux [cf. Eq. (3)], and $\langle n_{B_2}(R) \rangle \simeq (n_{B_2}^0 + n_{B_2}^1)/2$ the average B_2 concentration near the surface. Using Eq. (9), we get

$$\tau_- = \tau_+(W_{max} - 2\langle J_{B_2} \rangle)/(2\langle J_{B_2} \rangle - W_{low}). \qquad (10)$$

Equation (8) indicates that τ_+ is independent of geometry. This conclusion is correct if the reaction rate during the high-reactive period is much higher than the average diffusion flux. In reality, these values are often comparable. In the latter case, τ_+ will depend on R, but this dependence is expected to be weak. On the other hand, the dependence of τ_- on R is relatively strong because $\langle J_{B_2} \rangle$ in Eq. (10) is dependent on R. To estimate τ_- in the 1D or 2D cases, one can also use Eq. (10) (the only difference is that in the expression for $\langle J_{B_2} \rangle$ one should replace R by the length characterizing the concentration gradients in the case under consideration).

Typical oscillatory kinetic curves obtained by numerically integrating the diffusion equation for the B_2 concentration (we employed the Crank-Nicholson method [10]) are shown in Fig. 2. In this example, the calculations indicate that the reactive and unreactive periods are 0.38 and 1.14 s, respectively. On the other hand, Eqs. (8) and (10) yield $\tau_+ = 0.11$ and $\tau_- = 0.22$ s. Thus, the analytical estimates are in reasonable agreement with numerical calculations (the difference is
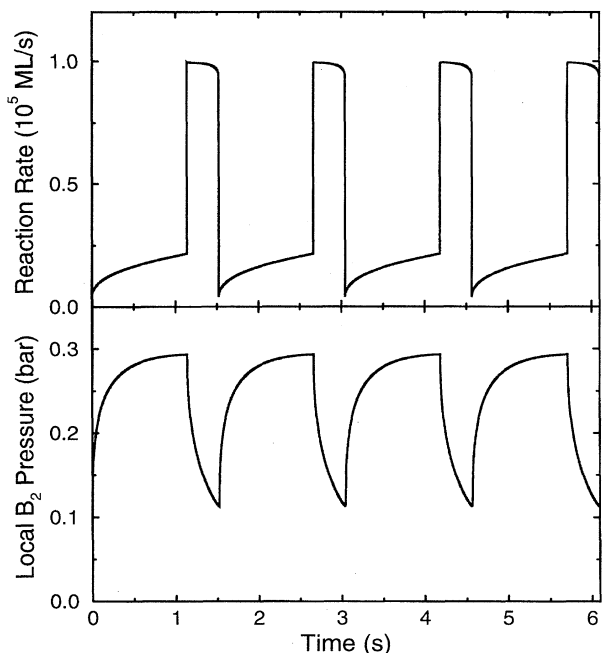
FIG. 2. Reaction rate and B_2 pressure near the surface as a function of time (according to numerical calculations with parameters presented in Table I).

connected with the fact that for the chosen set of parameters the reaction rate in the high-reactive state is comparable with the average diffusion flux).

Changing the values of the governing parameters, we may reach regions where the necessary conditions for generation of sustained oscillatory kinetics are not fulfilled. Our numerical studies, which will be presented elsewhere [11], show that in these regions one can obtain *damped* oscillations (with increasing time, the period of oscillations monotonically increases and then they disappear).

Above, we analyzed oscillatory kinetics resulting from mass-transfer limitations for B_2 molecules only. Diffusion of A molecules was considered to be rapid. If the transport of A is also limited significantly, but not too strongly (i.e., comparable to that for B_2), oscillatory kinetics are still possible as demonstrated by our numerical studies. On the other hand, if B_2 diffusion is very fast, one can verify that oscillations are always lacking for the kinetics given by Eqs. (1) and (2).

Our study identifies a type of isothermal oscillatory chemical reactions, caused by the coupling of nonoscillatory surface kinetics with diffusion limitations in the gas phase. The phenomenon may be searched for in real systems exhibiting bistability. Referring to Fig. 1(a), we note that a favorable condition is when the gas mixture is deficient in B_2 (from a stoichiometry point of view). Exploring CO or hydrogen oxidation on Pt (when CO or H_2 are identified with A, and O_2 with B_2 [7]), we find that the mass-transfer limitations for O_2 are minor compared to those for CO or H_2 (because the bistability occurs in large oxygen excess) and conclude that the mechanism described is not expected to show up in these systems. The conditions for diffusion-driven isothermal oscillations should thus be looked for in other rapid heterogeneous reactions.

We finally note that the type of oscillatory behavior identified need not be restricted to a catalytic reaction, which was the explicit example used above. Reactions between two or more reactants where the kinetics is confined to a surface and transport is occurring through a surrounding gas or liquid are much more general. Examples are chemical vapor deposition and other layer growth processes at surfaces, surface etching, electrochemistry and regulatory processes at biological surfaces, to name a few.

[1] P. Gray and S.K. Scott, *Chemical Oscillations and Instabilities* (Clarendon, Oxford, 1990).

[2] G. Ertl, Adv. Catal. **37**, 231 (1990); R. Imbihl and G. Ertl, Chem. Rev. **95**, 697 (1995).

[3] (a) L.F. Razon and R.A. Schmitz, Catal. Rev.-Sci. Eng. **28**, 89 (1986); (b) F. Schüth, B.E. Henry, and L.D. Schmidt, Adv. Catal. **39**, 51 (1993).

[4] G. Ertl, P.R. Norton, and J. Rüstig, Phys. Rev. Lett. **49**, 177 (1982).

[5] H. Levine and X. Zou, Phys. Rev. E **48**, 50 (1993); M. Falcke

and H. Engel, J. Chem. Phys. **101**, 9903 (1994); F. Mertenes, R. Imbihl, and A. Mikhailov, *ibid.* **101**, 9903 (1994).

[6] J.W. Evans, Langmuir **7**, 2514 (1991).

[7] V.P. Zhdanov and B. Kasemo, Surf. Sci. Rep. **20**, 111 (1994).

[8] V.P. Zhdanov, Phys. Rev. E **50**, 760 (1994).

[9] V.P. Zhdanov and B. Kasemo, Appl. Surf. Sci. **74**, 147 (1994).

[10] W.H. Press, S.A. Teukolsky, W.T. Vetterling, and B.P. Flannery, *Numerical Recipes in C* (University Press, Cambridge, 1994), Chap. 19.2.

[11] D. Kulginov, V.P. Zhdanov, and B. Kasemo (unpublished).