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First-order kinetic phase transitions in simple reactions on solid surfaces: Nucleation and growth of the stable phase

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First-order kinetic phase transitions connected with bistability and resulting in chemical waves are experimentally observed in rapid surface reactions such as CO or hydrogen oxidation on transition metals. If in this case the system exhibiting bistability is initially in the metastable state, the transition to the stable state occurs via nucleation and growth of the stable kinetic phase. We estimate the rate of this process, assuming that nucleation results from fluctuations in the arrangement of adsorbed particles due to surface diffusion.

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In analogy to real thermodynamic phase transitions, the term "kinetic phase transition" physically means that the kinetic behavior of the system under consideration changes qualitatively when a control parameter (e.g., temperature or pressure) passes through a critical point. Mathematically, this means that a bifurcation occurs at this point. If the change in the reaction rate is stepwise at the critical point, the kinetic phase transition belongs to the first-order class. If the change is softer, the transition is continuous.

The first-order kinetic phase transitions connected with bistability and resulting in chemical waves are experimentally observed in rapid surface reactions such as CO or hydrogen oxidation on transition metals under UHV conditions, and at atmospheric pressure as well [1–3]. Continuous kinetic phase transitions in heterogeneous reactions have been predicted for system with a high reaction rate, provided that the adsorbed species are immobile (see the reviews [2,3]). In real systems, however, surface diffusion is usually rapid compared to reaction steps. Perhaps this is the main reason why continuous kinetic phase transitions have not been observed so far.

The first-order kinetic phase transitions can be described by common, mean-field kinetic equations. For example, the well established mechanism of CO oxidation on Pt(111), at high-vacuum conditions, contains reversible monomolecular CO adsorption, irreversible oxygen adsorption, and CO+O reaction between adsorbed species to form product CO_2 molecules which desorb rapidly. The corresponding mean-field equations are as follows [1]:

$$d\Theta_{CO}/dt = k_1 P_{CO}[1-(\Theta_{CO}/\Theta_{CO}^s)^2] - k_2\Theta_{CO} - k_3\Theta_{CO}\Theta_O \, , \tag{1}$$

$$d\Theta_O/dt = k_4 P_{O_2}[1-\Theta_{CO}/\Theta_{CO}^s - \Theta_O/\Theta_O^s]^2 - k_3\Theta_{CO}\Theta_O \, , \tag{2}$$

where $\Theta_{CO}^s = 0.5$ and $\Theta_O^s = 0.25$ are the saturation coverages. Equation (1) takes into account that the coverage dependence of the CO sticking coefficient is weak up to saturation (which is suggested to be due to a precursor mechanism of adsorption). The model also takes into account that preadsorbed CO inhibits dissociative adsorption of oxygen and that no such site-blocking effect is exerted by adsorbed oxygen for incoming CO molecules.

At steady-state conditions, one can express Θ_O via Θ_{CO} by employing Eq. (2) and then solve Eq. (1) for Θ_{CO}. This equation has one or three solutions for the CO coverage (Fig. 1). In the latter case, the intermediate solution (with respect to absolute coverage) is unstable and the other two solutions are stable. Thus, if the temperature is not too high, the model presented by Eqs. (1) and (2) predicts a bistable reaction regime and hysteresis for $P_{CO}^1 \le P_{CO} \le P_{CO}^0$ (P_{CO}^0 and P_{CO}^1 are the critical CO pressures at a given temperature and oxygen pressure). In this regime, one stable solution corresponds to the surface covered predominantly by oxygen (the reaction rate is high) and the other to the surface covered predominantly by CO (the reaction rate is low). These solutions are stable if one employs the mean-field approximation and does not take into account fluctuations of adsorbate coverages due to surface diffusion.

When considering the effect of surface diffusion, a new important parameter P_{CO}^* ($P_{CO}^1 < P_{CO}^* < P_{CO}^0$) should be introduced, corresponding to equistability of the different kinetic phases. In the bistable region, the oxygen-domination regime is absolutely stable for $P_{CO} \le P_{CO}^*$ and metastable at $P_{CO}^* < P_{CO} \le P_{CO}^0$. The CO-domination regime is metastable at $P_{CO}^1 \le P_{CO} < P_{CO}^*$ and absolutely stable at $P_{CO} \ge P_{CO}^*$. Physically, the parameter P_{CO}^* is directly connected with calculating the velocity of chemical waves. If, for example, at a given value of P_{CO} ($P_{CO}^1 < P_{CO} < P_{CO}^0$), one part of the surface, initially covered primarily by CO, and the other part, corresponding to the "reactive" state, are separated by a linear interface, then with increasing time the interface will move from the low-rate region to the high-rate region, or in the opposite direction, due to diffusion and reaction (this is a chemical wave). In the former case, the velocity of the

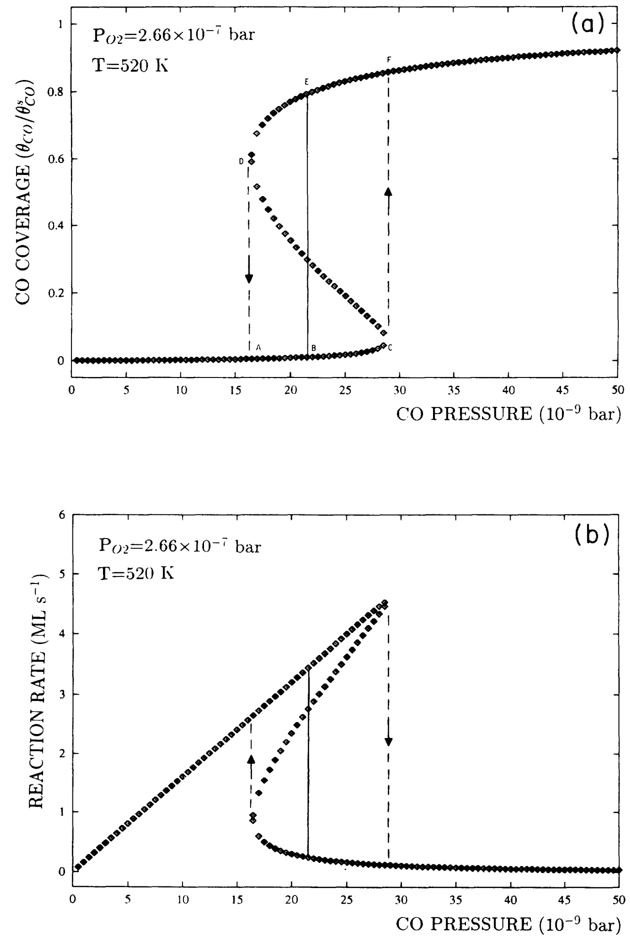

FIG. 1. (a) CO coverage and (b) reaction rate (monolayer per second) as a function of CO pressure [according to Eqs. (1) and (2) with the rate constants from Ref. [1]]. Pointers indicate a hysteresis loop. The solid lines show a stepwise transition corresponding to the equistablity criterion [Eq. (3)].

chemical wave is positive, $v>0$, the low-rate regime is stable, while the reactive regime is metastable. If $v<0$, the situation is the reverse. Thus equistablity of the two kinetic phases occurs only for $v=0$.

A chemical wave, realizing the transition from the metastable kinetic phase to the stable state and moving at a velocity v, is given by a special solution, $\Theta=\Theta(\xi)$ with $\xi=x-vt$, to the diffusion equation for CO molecules (oxygen diffusion is negligible compared to CO diffusion),

$$\partial\Theta/\partial t=D\partial^2\Theta/\partial x^2+W(\theta) ,$$

where Θ is the CO coverage (we omit here the subscript CO), D the CO diffusion coefficient, and $W(\Theta)$ the right-hand part of Eq. (1) [the oxygen coverage is assumed to be given by the steady-state solution of Eq. (2)]. The well-known relationship between v and $\Theta(\xi)$ is as follows [1,3,4]:

$$v=\int_{\Theta_1}^{\Theta_3}W(\Theta)d\Theta\Big/\int_{-\infty}^{+\infty}(d\Theta/d\xi)^2dx ,$$

where Θ_1 and Θ_3 are the steady-state solution to Eq. (1). Accordingly, the equistability criterion ($v=0$) can be written as

$$\int_{\Theta_1}^{\Theta_3}W(\Theta)d\Theta=0 . \tag{3}$$

A metastable kinetic phase is unstable only with respect to sufficiently strong perturbations. If a large nucleus of stable phase is created inside a metastable domain, this nucleus starts to grow and then initiates chemical waves. The radius of a critical nucleus that can grow can be estimated by analyzing the front propagation in polar coordinates. In this case, the change in the front velocity due to a finite value of the front radius R is given by [1,3,4]

$$v(R)\approx v-D/R , \tag{4}$$

where v is the front velocity for a linear interface (i.e., for $R\to\infty$). For a critical nucleus, $v(R)$ is equal to zero, and accordingly

$$R_{\rm cr}\approx D/v . \tag{5}$$

For CO oxidation on Pt, we have $v\sim(DP)^{1/2}$ and $R_{\rm cr}\sim(D/P)^{1/2}$, where P is the reactant pressure [1,3].

If the system under consideration is initially in the metastable state, the nucleation and growth of islands of the stable kinetic phase will result in the transition to the stable state. Our goal is to evaluate the rate of this transition, assuming that (i) the surface is perfect (i.e., any defects are absent), and (ii) nucleation is connected with fluctuations in the arrangement of adsorbed particles due to surface diffusion (a similar problem for diffusionless first-order kinetic phase transitions has recently been discussed in Refs. [5,6]).

To simplify our analysis, we will characterize the nuclei of the stable phase only by their radius R. The nucleus radius is a fluctuating value. On average, the evolution of R can be approximated as [cf. Eq. (4)]

$$\langle dR/dt\rangle=v(R)\approx\begin{cases}-D/R , & R<R_{\rm cr} \quad (6)\\ v , & R>R_{\rm cr} . \quad (7)\end{cases}$$

In the framework of this approximation, all the nuclei passing through the critical radius grow with the velocity v. On the other hand, the subcritical nuclei are dissolved on average. By analogy with the kinetics of thermodynamic first-order phase transitions [7], we will employ the Fokker-Planck equation for describing the time dependence of the radius distribution $f(R)$ of the subcritical nuclei

$$\partial f/\partial t=-\partial J/\partial R , \tag{8}$$

where

$$J=-B\partial f/\partial R+Af \tag{9}$$

is the flux in the "radius space." The coefficient A in Eq. (9) is directly connected with $\langle dR/dt\rangle$, i.e. [7],

$$A=v(R) . \tag{10}$$

The relationship between A and B can be derived taking into account that the flux, given by Eq. (9), should be equal to zero for the "equilibrium" distribution of nuclei $f_0(R)$ in the metastable state. The latter distribution can be constructed assuming the adsorbed particles in the metastable state to be located at random. If, for example, the metastable state is on the line between points B and C and the stable state is on the line between points E and F [Fig. 1(a)], then the CO coverage is low in the metastable and high in the stable state, respectively. In this case, it is reasonable to identify the nuclei of the stable phase introduced above phenomenologically with the CO "percolation" clusters (by definition, all the CO molecules within one cluster are connected to each other by nearest-neighbor links). This idea looks reasonable even provided that the arrangement of adsorbed particles in the critical nuclei is not necessarily "compact."

If s is the number of CO molecules in a given cluster, the cluster radius can be defined in the case of simple lattices via the relationship

$$s=\pi R^2/S_0 , \tag{11}$$

where S_0 is the area of the elementary cell. From the site percolation theory [8,9], the number of large clusters is known to be given by

$$n_s \approx Qs^{-1}\exp(-\beta s) . \tag{12}$$

The parameter β in this equation depends on coverage. In particular,

$$\beta \approx -\ln(\lambda\Theta) \tag{13}$$

at low coverages, and $\beta \rightarrow 0$ at $\Theta \rightarrow \Theta_c$, where Θ_c is the percolation threshold. The parameters λ and Θ_c are dependent on the type of lattice. For triangular, square, and honeycomb lattices, $\lambda=5.19$, 4.06, and 3.04 [8], and $\Theta_c=0.5$, 0.593, and 0.696 [9], respectively. The parameter Q in Eq. (12) can be estimated from the normalization condition

$$\sum_s sn_s=\Theta N_0 , \tag{14}$$

where N_0 is the number of sites per unit area. Substituting expression (12) into Eq. (14) yields

$$Q\approx\beta\Theta N_0 . \tag{15}$$

Employing Eqs. (11) and (12), we obtain the following expression for the "equilibrium" distribution of nuclei in the metastable state:

$$f_0(R)\approx(2Q/R)\exp(-\pi\beta R^2/S_0) . \tag{16}$$

Then, the relationship between the coefficients A and B can be derived by substituting expression (16) into Eq. (9), differentiating only the exponent, and setting $J=0$. After these steps, we have

$$B=-AS_0/2\pi\beta R ,$$

or, employing Eq. (10) for A and Eq. (6) for $v(R)$,

$$B=DS_0/2\pi\beta R^2 . \tag{17}$$

The radius distribution of the subcritical nuclei can be represented as

$$f(R)=\chi(R)f_0(R) , \tag{18}$$

where the function $\chi(R)$ should be chosen so that the flux in the radius space given by Eq. (9) is constant (this requirement corresponds to the steady-state approximation for the nucleation kinetics [7]). In addition, we can employ the following boundary conditions:

$$\chi(R)=\begin{cases}1 & \text{at } R\rightarrow 0 \qquad (19)\\ 0 & \text{at } R\rightarrow R_{\text{cr}} . \qquad (20)\end{cases}$$

Equation (19) guarantees that $f(R)$ is close to $f_0(R)$ at small R. Condition (20) corresponds to the assumption that all the nuclei passing through the critical radius grow with the velocity v [Eq. (7)] and do not decay back.

Substituting expression (18) into Eq. (9) yields

$$\partial\chi/\partial R=-J/Bf_0 .$$

Integrating this equation with condition (20), we get

$$\chi(R)=J\int_R^{R_c}(1/Bf_0)dR .$$

The second boundary condition [Eq. (19)] is fulfilled if

$$J=1\Big/\int_0^{R_c}(1/Bf_0)dR .$$

Inserting into this equation expressions (16) and (17) and integrating, we obtain for the flux in the radius space

$$J\approx(2QD/R_c^2)\exp(-\pi\beta R_c^2/S_0) ,$$

or, taking into account Eq. (15),

$$J\approx(2\beta\Theta N_0 D/R_c^2)\exp(-\pi\beta R_c^2/S_0) . \tag{21}$$

In the framework of the steady-state approximation, the flux in the radius space is equal to the nucleation rate. Thus Eq. (21) gives us the nucleation rate. The fraction of the surface covered by the stable phase, $\mathcal{P}$, is then defined by the well-known Avrami equation [10]

$$\mathcal{P}=1-\exp(-\pi Jv^2t^3/3) . \tag{22}$$

Accordingly, the time characterizing the growth process is

$$\tau\approx 1/(Jv^2)^{1/3} ,$$

or, taking into account Eq. (21),

$$\tau\approx(R_c^2/\beta\Theta N_0 Dv^2)^{1/3}\exp(\pi\beta R_c^2/3S_0) . \tag{23}$$

The equations above have been derived for describing the transition from the metastable state on line BC to the stable state on line EF [Fig. 1(a)]. In this case, the CO coverage Θ is low in the metastable and high in the stable phase. If one analyzes the transition from line DE to line AB, the situation is the opposite, i.e., the CO coverage is high in the metastable and low in the stable phase. In the latter case, the nuclei of the stable phase will be formed not by CO molecules but by the sites which are free of CO. Accordingly, applying Eqs. (21)–(23), one should replace Θ by $(1-\Theta)$.

Finally, it is of interest to make some elementary estimates. At $P \approx 10^{-7}$ bar and $T \approx 500$ K, we have $D \approx 10^{-7}$ cm^2/s, $v \approx 10^{-3}$ cm/s, and $R_{\rm cr} \approx 10^{-4}$ cm [1]. In addition, $N_0 \approx 10^{15}$ cm^{-2} and $S_0 = 1/N_0 \approx 10^{-15}$ cm^2. With these values, the preexponential factor in Eq. (23) is about 10^{-3} s (the parameters β and Θ in the preexponential factor can be neglected). For the transition from the metastable state on line BC to the stable state on line EF [Fig. 1(a)], the CO coverage is very low in the metastable phase, and accordingly $\beta > 1$. In this case, the exponential factor in Eq. (23) is so large that the spontaneous nucleation on the flat surface is in fact completely negligible. For the transition from line DE to line AB, the parameter β may be lower, but anyway this parameter is not able to compensate the large value of the ratio $\pi R_c^2/3S_0$. Thus, for CO oxidation on Pt at low pressures, the nucleation seems to occur only on defect sites, e.g., on steps. With increasing pressure, the critical radius decreases, $R_c \sim 1/P^{1/2}$ [1,3], and the situation for spontaneous nucleation on the perfect sites of the surface may be more favorable.

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