KINETIC INSTABILITIES IN HETEROGENEOUSLY CATALYZED REACTIONS—I

RATE MULTIPLICITY WITH LANGMUIR-TYPE KINETICS

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Abstract—The question under which conditions kinetic instabilities can be described by Langmuir type kinetics is studied using a fairly general model for the surface reaction


\[ pA + qB \rightarrow C. \]

This paper is concerned with the occurrence of rate multiplicities (ignition-extinction phenomena). It is shown that rate multiplicity can be caused by the competing chemisorption of \( A \) and \( B \) upon the same active sites of the catalyst. Rate multiplicity can occur if at least one of the chemisorption or reaction steps is of second order. No rate multiplicity can be expected, if either \( A \) or \( B \) reacts via an Eley–Rideal type mechanism.

INTRODUCTION

During the last decade much attention has been devoted to stability problems in chemical reactors. Only recently the interest shifted from thermally induced instabilities to kinetic instabilities. This shift was induced by experimental results of Wick and cols. concerning the CO oxidation on platinum which clearly demonstrated that ignition-extinction phenomena as well as periodic oscillations can occur under isothermal conditions and under the exclusion of mass transfer limitations [1-3].

In the mean time a number of additional experimental results on kinetically induced instabilities as well as theoretical attempts to model these effects have been published, most of which are condensed in a comprehensive review by Sheintuch and Schmitz [4].

It is now well known that kinetic instabilities can occur in a number of surface reactions on transition metals involving oxygen [1, 2, 5-7] but it is still unsettled as to how these instabilities should be described in terms of a kinetic model. Belyaev and Slinko [5], Pikios and Luss [8] and Schmitz and Sheintuch [4] favor the assumption that the instabilities are brought about by variations of the activation energies in some of the surface reaction steps with surface coverage. This means that in case of isothermal reactions some rate constants have to change exponentially with surface coverage. In the example discussed by Belyaev and Slinko as well as by Pikios and Luss it had to be assumed that the rate constant for the surface reaction between chemisorbed oxygen and chemisorbed hydrogen decreased exponentially with the concentration of chemisorbed oxygen—a supposition which is somewhat unusual for the catalytic hydrogen oxidation.

It is the purpose of this contribution to show that rather simple Langmuir type kinetics can as well be used to model the observed kinetic instabilities. The necessary conditions for the occurrence of instabilities are studied analyzing a fairly general surface reaction scheme. Base of this study and starting point for the kinetic models are the experimental results and the modelling assumptions proposed by Wick et al. [1, 9].

Heterogeneously catalyzed surface reactions are usually described by multistep mechanisms considering chemisorption, reaction and desorption of the reacting species. The complete consideration of these steps leads to rather complex kinetic models in which an overall-reaction rate usually cannot be specified explicitly.

This is the reason why generally the Langmuir–Hinshelwood or Hougen–Watson-type approach to surface reactions is used which is based upon the assumption of equilibrium for all but one step and usually leads to explicit (unique) reaction rate expressions.

Yet if reaction rate multiplicity, i.e. ignition-extinction phenomena are observed, the underlying reaction rate expression has to be implicit to possess multiple solutions. For the case of a surface reaction this implies that at least two surface reaction steps have to be in non-equilibrium. Based upon these considerations, reaction rate multiplicity will be studied for the general surface reaction


\[ pA + qB \rightarrow C. \]

in this contribution.

The best-known example of oscillatory instabilities in chemical engineering is the occurrence of limit cycles in a cooled CSTR with an exothermic reaction. This type of instability can be considered a quasi-harmonic oscillation between a heat storage and a concentration storage [10]. The oscillations observed with the CO- and \( \text{H}_2 \)-oxidation on platinum however often had the character of relaxation oscillations. This class of oscillations can be interpreted by the combination of one storage element with a switching device which changes the direction of the current to or from the storage. In this respect relaxation
oscillations are basically different from quasi-harmonic oscillations between two storage elements. In chemical reactions the switching characteristic, necessary for the occurrence of relaxation oscillations, can be brought about by a non-unique reaction rate dependency (switching between ignition and extinction of the reaction). Based upon these considerations an analysis of oscillatory instabilities in heterogeneously catalyzed reactions is given in Part II of this paper. Applications of the obtained results to the CO-oxidation on Pt are given elsewhere [15].

**RATE MULTIPlicity—AN INTRODUCTORY EXAMPLE**

It seems best to start the discussion of multiple reaction rates with a simple example [11]. Consider the surface reaction

\[ 2A + B \rightarrow 2C \]

and assume that it proceeds via the following steps

\[ A + X \overset{1}{\rightarrow} AX \]  \hspace{1cm} (1)

\[ B + 2X \overset{2}{\rightarrow} BX_2 \]  \hspace{1cm} (2)

\[ 2AX + BX_2 \overset{3}{\rightarrow} 2C + 4X \]  \hspace{1cm} (3a)

where \( X \) stands for active site. If step 2 is in equilibrium and \( k_2 \gg k_2[B] \) (i.e. the concentration of \( BX_2 \) is always very low) then the mechanism can be approximated by

\[ A + X \overset{1}{\rightarrow} AX \]  \hspace{1cm} (1)

\[ 2AX + B + 2X \overset{3}{\rightarrow} 2C + 4X. \]  \hspace{1cm} (3b)

Step (1) and (3b) are in non-equilibrium and there is a strong autocatalytic feedback in step (3b).

In the steady state and with normalized surface concentrations \( [X] = 1 - [AX] \), the reaction rate of \( A, r_A \), is

\[
\frac{r_A}{r_C} = \frac{k_1[A] - [AX] (k_1[A] + k_{-1})}{2k_1[B][AX]^2(1 - [AX])^2}.
\]

Following a similar treatment of Wicke et al. [1, 9], the steady state may be considered as equilibrium between the rate of chemisorption \( r_C([AX]) \) and the rate of reaction \( r_R([AX]) \). This is shown in Fig. 1. Depending upon the values of the rate constants either a unique rate dependency (Fig. 1b) or reaction rate multiplicity (Fig. 1a) can be obtained. An analysis shows that multiple solutions occur if

\[
k_{-1} < \frac{\sqrt{12} - 3}{18} k_2[B] = 0.0285 k_2[B].
\]

The rate dependencies obtained are in qualitative agreement with experimental findings for the CO-oxidation on Pt. Unique rate dependencies (Fig. 1b) have been found at low temperatures and for low to medium active catalysts [2, 12, 13], rate multiplicity as in Fig. 1a can be obtained. A shift from the region of unique rates at low temperatures to that of multiple rates at higher temperatures is easily incorporated in the model if it is assumed that the reaction step (3) is more activated than the desorption of \( AX(E_3 > E_{-1}) \).

![Fig. 1](image-url)  
Fig. 1. Steady state rate dependency resulting from equality between the rate of chemisorption \( r_C \) and the rate of surface reaction \( r_A \) (from [11]).
The above example shows that a rather simple mechanism for a surface reaction is sufficient to produce multiple solutions.

The reaction $pA + qB \rightarrow C$

To obtain a better understanding under which conditions reaction rate multiplicity can be expected, a more general surface reaction will now be considered. It is assumed that the overall reaction $pA + qB \rightarrow C$ (5) proceeds via the following surface reaction steps:

$$A + nX \rightarrow AX_n$$ (6)

$$B + mX \rightarrow BX_m$$ (7)

$$pAX_n + qBX_m \rightarrow CX_i + \left( np + mq - l \right) X$$ (8)

$$CX_i \rightarrow C + lX.$$ (9)

It should be mentioned that this mechanism includes not only Langmuir steps (chemisorption-reaction-desorption) but also Eley–Rideal type steps (reaction of one component directly from the gas-phase). If for example $m = 0$ in step (7), $B$ reacts via an Eley–Rideal type mechanism.

The influence of $p$ and $q$

The method of analysis will be outlined considering the influence of the coefficients $p$ and $q$. (A more detailed derivation can be found in [15]). If $n = m = l = 1$, and equilibrium is assumed for the C-desorption (step (9)), the steady state form of balance equations (10) and (11) can be reduced to the following algebraic equation for $AX$:

$$\frac{d[AX]}{dt} = b_1 \left( k_{-1}[AX] \right) - b_1 [AX]$$ (10)

$$\frac{d[BX]}{dt} = b_2 \left( k_{-2}[AX]^p \right) - b_2 [BX]$$ (11)

$$\frac{d[CX]}{dt} = k_{-3}[C][X] - k_{-4}[CX] + k_{-4}[CX]^q - k_{-3}[CX]^q$$ (12)

with the normalized empty site density

$$[X] = 1 - n[AX_n] - m[BX_m] - l[CX_i].$$ (13)

It will be assumed that the gas phase concentrations are kept constant. In the steady state the time derivatives are equal to zero. But the resulting system of algebraic equations is still so complex, that a general analysis is not feasible. A number of special cases will be considered instead. They are obtained under the aforementioned assumption that at least two of the four reaction rate steps (6)–(9) have to be in non-equilibrium. The basic problem to be discussed is the influence of the stoichiometric coefficients $l$, $m$, $n$, $p$ and $q$ upon the occurrence of reaction rate multiplicity.

Equation (14) can be interpreted geometrically as in the introductory example. Again the left-hand side is a chemisorption line $r_c$ (linear in $[AX]$) and the right-hand side $r_R = r_{R1} + r_{R2}$ is a reaction rate curve. In the case $pk_{-2} > - a$ (16) all $b_i$ are positive and rate multiplicity can occur if the chemisorption line $r_c$ cuts the reaction rate curve $r_R$ in more than one point (Fig. 2). This leads to the following necessary conditions for rate multiplicity:

(i) $a > qk_{-1}$, (otherwise $r_{R1}$ is monotonically increasing).
(ii) $q \geq 2$, (otherwise $r_{R1}$ has no inflection point after the maximum).

In addition $k_{-1}$,$x_1$ has to be sufficiently small and $x_1 \approx x_2 = 1$ where

$$x_1 = \frac{pk_{-2}}{pk_{-2} + qk_{-1}} \quad \text{and} \quad x_2 = \frac{a}{a - qk_{-1}}.$$ (17)
is identical with the first one if \( A \) is replaced by \( B \), \((n, p)\) by \((m, q)\) and \((k_1, k_{-1})\) by \((k_2, k_{-2})\), since \( A \) and \( B \) are obviously equivalent in the rate mechanism eqns (6)-(8).

The result obtained implies that in the case \( m = n = l = 1 \) combinations of the rate constants leading to reaction rate multiplicity can always be found provided that \( q \geq 2 \), \( p > 0 \) or (considering the above stated equivalence) \( p \geq 2 \), \( q > 0 \).

**The influence of \( n \) and \( m \)**

The influence of \( n \) and \( m \) on rate multiplicity can be discussed conveniently by considering the special case where the \( B- \) and \( C\)-chemisorption (steps (7) and (9)) are in equilibrium and \( k_2[B] \ll k_{-2} \). The analysis (see [15] for details) leads to the result that reaction rate multiplicity can occur if

\[
mq > n, \quad n \geq 1
\]

or

\[
np > m, \quad m \geq 1.
\]

This means that any reaction mechanism where only one of the stoichiometric coefficients \( m, n, p, q \) is greater than one is a potential candidate for rate multiplicity.

If however \( m \) or \( n \) are equal to zero, i.e. an Eley-Rideal type mechanism is considered for either \( A \) or \( B \), it can easily be shown that only unique steady state solutions are possible.

**The influence of product desorption**

So far instability effects have been brought about by the combination of \( A \)- and \( B\)-chemisorption together with reaction. Product desorption had been considered in equilibrium and played only a secondary role. However, if product desorption is of decisive importance for the occurrence of rate multiplicity it should also demonstrate its influence in cases which have so far given only unique solutions, i.e. in the case \( m = n = p = q = 1 \) or in the case that either \( A \) or \( B \) reacts via an Eley-Rideal type mechanism. The analysis reveals that in both cases multiple solutions can be excluded as long as the reaction proceeds from \( A \) to \( C \) [15].

**PHYSICAL INTERPRETATION**

In the examples considered, components \( A \) and \( B \) of the reaction mixture were competing for the same type of active sites. Therefore a general rate dependency as depicted in Fig. 3 must be expected. The reaction rate passes through a maximum since, with increasing concentration, \( A \) tends to displace \( B \) from the surface. In the limit \( [A] \to \infty \) the whole surface is blocked with \( AX \), and no reaction can proceed. Under realistic conditions however \( [A] \) cannot be increased arbitrarily and a rate maximum will only occur if the chemisorption velocity of at least one of the components at its highest concentration exceeds its desorption velocity considerably (here: \( k_1[A]_{\text{max}} \gg k_{-1} \)). Otherwise no blocking of the surface can take place. Since desorption usually is a much more activated process as compared to chemisorption, blocking of the surface can be expected only at low and medium temperatures.

After a rate maximum a rapid decrease in the rate will take place if the consumption of \( BX \) in the reaction step is greater than the consumption of \( AX \) or if \( B \) needs more active sites than \( A \) to chemisorb \((mq > n, \text{ eqn 18a})\). This may lead to a sudden extinction of the reaction and gives rise to a rate dependency as depicted in Figs. 1(a) and 4(a). Since the strong chemisorption of \( A \) is responsible, this type of instability will be referred to as being induced by \( A\)-blocking of the surface.

A different rate dependency will be expected if \( B \) is strongly chemisorbed at the surface \((k_{BL} \gg k_{-2})\). This case will be referred to as \( B\)-blocking of the surface. With low concentrations of \( A \) the surface is completely occupied with \( B \) and \( A \) finds few places to chemisorb and react. The rate progresses only slowly with \([A]\). But if \( [AX] \) increases more than \([BX] \) \((np > m, \text{ eqn 18b})\), a sudden ignition of the reaction may take place (Fig. 4b). (The subsequent decrease of the rate is again due to \( A \) occupying the surface and displacing \( B \).)

If however \( m \) or \( n \) are equal to zero (i.e. an Eley-Rideal type mechanism is assumed for either \( A \) or \( B \)), blocking of the surface has no effect upon the rate and hence no instabilities can be expected.
Instabilities due to A-blocking or B-blocking can be considered special cases of self-retarding and autocatalytic reactions. It should be noted however that self-retardation implies autocatalytic behaviour and vice versa. If, in the “A-blocking”-case the gasphase concentration $[B]$ is changed instead of $[A]$, a rate dependency like the one depicted in Fig. 4(b) results.

A numerical example

The results obtained will be discussed considering a numerical example. As in the introduction a reaction

$$2A + B \rightarrow 2C$$

consisting of the following three steps will be considered:

$$A + X \underset{1}{\overset{2}{\rightleftharpoons}} AX$$

$$B + mX \rightarrow BX_m$$

$$2AX + BX_m \rightarrow 2C + (2 + m)X.$$  \hfill (19)

No equilibrium assumptions are used now. The steady state behaviour depends upon the four parameters $k_{13}[A] = k_1[A]/k_3$, $k_{-13} = k_{-1}/k_3$, $k_{23}[B] = k_3[B]/k_5$ and $k_{-23} = k_{-2}/k_5$. In the following pictures the reduced rate $r = r_\text{sl}(2k_3) = |AX|^2|BX_m|$ is plotted vs $k_{13}[A]$.

Rate multiplicity due to A-blocking can be expected if $k_{-13} \ll k_{13}[A]_{\text{max}}$, but only for $m \geq 2$. Figure 5 shows three characteristic cases: In Fig. 5(a) all necessary conditions are fulfilled and the resulting rate dependency is similar to the one obtained in the introductory example. In Fig. 5(b) $m$ is set to one and in Fig. 5(c) $k_{-13}$ is increased by a factor of 50. In both cases the above mentioned requirements are violated and no rate multiplicity is obtained.

Rate multiplicity due to B-blocking can occur if $k_{-23} \ll k_{23}[B]_{\text{max}}$ but only if $m = 1$. Figure 6 shows several cases; in Fig. 6(c) $m$ is set to $m = 2$, hence no multiplicity can be expected.

Also of interest is the region where both $k_{13} \ll k_{13}[A]$ and $k_{-23} \ll k_{23}[B]$ is fulfilled. Now the stoichiometric coefficient $m$ determines whether rate multiplicity due to A-blocking ($m = 2$, Fig. 7a and b) or due to B-blocking ($m = 1$, Fig. 7c) takes place.

CONCLUSIONS AND DISCUSSION

It has been shown that Langmuir type kinetics can lead to reaction rate multiplicity under fairly general conditions. Since the cause for this instability is the competitive chemisorption of (at least) two components at the same active sites, reaction rate multiplicity has been found if (and only if) the chemisorption velocity in a certain range exceeded the desorption velocity considerably. If this is the case for the species $A$ the instabilities have been called “induced by A-blocking”, if
it is the case for $A$, the cause of the instabilities was called "$B$-blocking". In the mechanism considered, $A$-blocking was found only if the stoichiometric coefficients fulfilled the conditions

$$mq > n \quad \text{and} \quad n \geq 1,$$

$B$-blocking only if

$$np > m \quad \text{and} \quad m \geq 1.$$

No rate multiplicity can be expected if either $A$ or $B$ reacts via an Eley-Rideal type mechanism (i.e. if $m$ or $n$ equals zero).

Since the CO oxidation on Pt represents the best studied example of rate multiplicity, a few conclusions concerning this reaction should be drawn.

It was frequently argued that the specific rate dependency of the CO oxidation may be due to a change from an Eley-Rideal to a Langmuir Hinselwood rate mechanism[12, 13, 18–21]. This supposition is in conflict with the above results. A mechanism as given in eqn (19) may be proposed instead, where \( m = 2 \) and \( A = \text{CO}, B = \text{O}_2 \). New, yet unpublished results of Wicke et al.[13, 14] show that the CO oxidation on Pt has a triangular rate dependency as depicted in Fig. 7(a) if isothermality and exclusion of mass transfer limitations can be assured.

An excess in the pellet temperature in the case of an exothermic reaction as well as diffusional resistance in the catalyst pores tends to increase the hysteresis between ignition and extinction considerably[14, 15]. As shown in the fundamental paper of Matsuura and Kato[16] as well as in subsequent contributions by Carberry[22] and Wei[17] the diffusional resistance may lead to rate multiplicity even with unique reaction rates of the Fig. 3 type.

**REFERENCES**

Kinetic instabilities in heterogeneously catalyzed reactions—I