

KINETIC INSTABILITIES IN CATALYTIC REACTIONS - A MODELLING APPROACH -

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During the past decade great effort has been directed towards the study of instabilities in chemical reactors. In the case of heterogeneously catalyzed reactions the main goal has been the investigation of temperature-induced instabilities. However, recent experimental studies of *Wloke* and co-workers with fixed bed reactors [1] and single catalyst pellets [2], and of *Hugo* and *Jakubith* with catalytic wires [3] have shown the ignition and extinction of the reaction and periodic oscillations which have to be considered induced by the kinetics of the surface reaction [7]. So far no detailed explanation of these instabilities in terms of a mathematical model has been made available. It is the purpose of this contribution to show under which conditions relatively simple Langmuir-type rate mechanisms exhibit steady state multiplicity as well as periodic instabilities and may serve as models for experimentally observed phenomena.

Steady state multiplicity

Consider the surface reaction $2A+B \rightleftharpoons 2C$. A mechanism for this reaction consists of a sequence of chemisorption and reaction steps, e.g.



where X stands for active site. For ease of representation let us assume that step (2) is in equilibrium, with the concentration of BXX always very low ($k_2 \gg k_2[B]$), and that the reaction step (3) is irreversible. Then, the mechanism reduces to



Now the autocatalytic character of step (4) is obvious, and one of the necessary conditions for kinetic instabilities, the presence of a positive feedback, is fulfilled. If the concentrations of the reactants in the gas phase are kept constant, only the concentration of chemisorbed A has to be considered. Its mass balance is:

$$\frac{d[AX]}{dt} = k_1[A][X] - \underline{k}_1[AX] - 2k_3[B][X]^2[AX]^2. \quad (5)$$

If the total number of active sites is set to 1,

$$[X] = 1 - [AX], \quad (6)$$

and the steady state mass balance is

$$\underbrace{k_1[A] - [AX](k_1[A] + \underline{k}_1)}_{r_C} = \underbrace{2k_3[B][AX]^2(1 - [AX])^2}_{r_R}. \quad (7)$$

Following a similar approach of *Wicke* and co-workers [2], the steady state may be considered as an equilibrium between the rate of chemisorption, r_C , and the reaction rate, r_R ($r_C = r_R = r_A$). This relations is shown in Fig. 1. As can be seen, it is easy to obtain r_A over $k_1[A]$. The reaction rate r_A increases almost linearly with $[A]$ at low concentrations and then passes through a maximum (r_{max}). Depending upon the ratio \underline{k}_1/r_{max} , two different cases can be distinguished. If this ratio is about or greater than one, a unique rate dependency $r_A = f([A])$ results (Fig. 1b). If, however, $\underline{k}_1 \ll r_{max}$, a region of multiple solutions exists which means that the reaction rate changes jumpwise at points of ignition and extinction (Fig. 1a). A reaction may show both rate dependencies at different temperatures if the activation energies for reaction and desorption, E_3 and E_1 , differ. If e.g. $E_3 > E_1$, Fig. 1a would correspond to high temperatures and Fig. 1b to low temperatures.

Two comments about the steady state multiplicity of the reaction rate seem in order:

- 1) In simple cases like this, the usual treatment of surface reactions with the assumption of equilibrium for all but one step leads to explicit (unique) rate laws

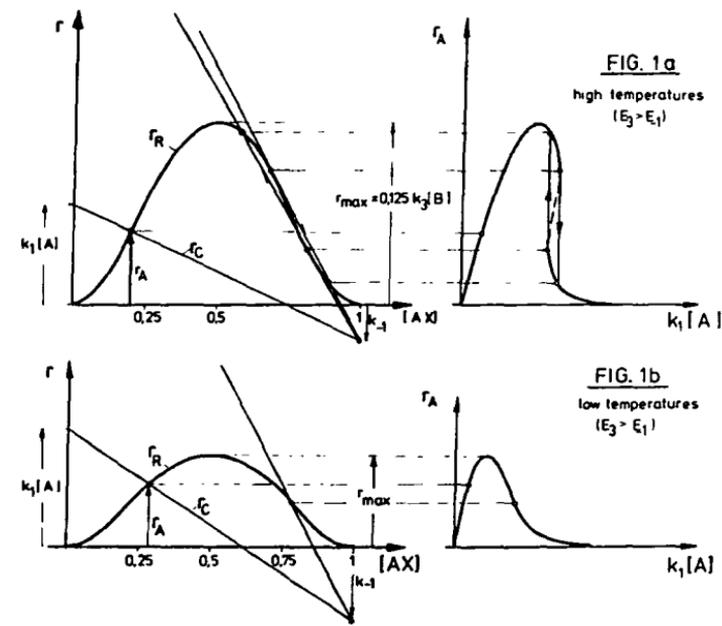


Fig. 1: Steady state dependency (equ. (7))

$r_A = f[A]$. Hence the assumption of equilibrium tends to conceal possible causes for instabilities in catalytic reactions.

- ii) The physical reason for the occurrence of rate multiplicity is the competitive chemisorption of A and B. An Eley-Rideal type mechanism where either A or B reacts directly from the gas phase will therefore show none of these instabilities.

Oscillations

The model, as it is, may be suitable to serve as an explanation for experimentally observed steady state multiplicity of the reaction rate, but is unable to exhibit oscillations. Such oscillations which frequently have the character of relaxation oscillations have been interpreted as periodic jumps between

the ignited and the extinguished steady state [2]. In our case the reaction will jump to the extinguished steady state if the AX-coverage on the surface is so high that a deficit occurs on empty sites and it will remain in the extinguished state if additional empty sites are not set free by some means. Hence all that is needed to produce a continuous succession of ignitions and extinctions is an additional step which provides (slowly) empty sites after extinction and which consumes (slowly) empty sites after ignition. A number of mechanisms may be considered for this purpose. Probably the most simple one is a "buffer" step where a component D from the reaction mixture chemisorbs reversibly at the surface



The enlarged model now consists of steps (1), (4) and (8) and the concentration of empty sites is

$$[X] = 1 - [DX] - [AX] = \alpha - [AX]. \quad (9)$$

It is convenient to write a balance equation for $\alpha = 1 - [DX]$ instead of $[DX]$. Then the new model is

$$\frac{d[AX]}{dt} = k_1[A]\alpha - (k_1[A] + k_{-1})[AX] - 2k_3[B][AX]^2(\alpha - [AX])^2, \quad (10)$$

$$\frac{d\alpha}{dt} = k_4[D][AX] + k_{-4} - \alpha(k_4[D] + k_4), \quad (11)$$

and the steady state

$$\underbrace{a k_1[A] - [AX] (a k_1[A] + k_{-1})}_{r_C'} = \underbrace{2k_3[B] a^2 [AX]^2 (1 - [AX])^2}_{r_R'}, \quad (12)$$

$$\text{where } a = \frac{1}{1 + k_4[D]}, \quad K_4 = \frac{k_4}{k_{-4}}. \quad (13)$$

This equation is equivalent to equ. (7) as plotted in Fig. 1 except for the factor a . Thus the steady state dependency of $r_A\{[A]\}$ will be comparable to the one discussed before.

Following the assumption that the oscillations are successive

switches between the ignited and the extinguished steady state brought about by the slow provision or consumption of empty sites, the instability can be modeled by equ. (11) and the quasisteady form of the AX-balance, equ. (10):

$$\underbrace{k_1[A] - [AX] \frac{(k_1[A] - k_{-1})}{\alpha}}_{r_C^*} = \underbrace{\frac{2k_3[B]}{\alpha} [AX]^2 (\alpha - [AX])^2}_{r_R^*} \quad (14)$$

Since r_{\max} is now equal to $r([AX] = \alpha) = 0.125k_3[B]\alpha^3$, the shape of the reaction rate curve r_R^* is strongly affected by α which, in turn, is controlled by balance equ. (11).

Using a similar graphical representation as before, the resulting behaviour is plotted in Fig. 2. Fig. 2a shows the graphi-

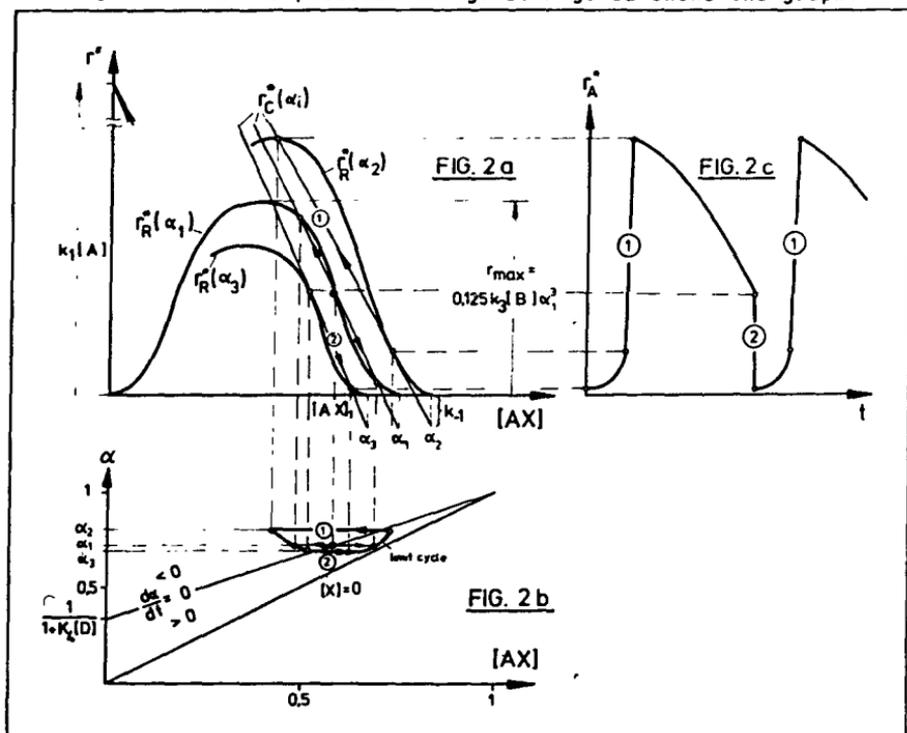


Fig. 2: The mechanism of oscillations on single pellets (equ. (11), (14))

cal representation of equ. (14) at different values of α . In Fig. 2b, α over $[AX]$ is plotted, and the steady state of equ. (11) ($\frac{d\alpha}{dt} = 0$) is marked together with regions for increasing and decreasing α . Let us start with the steady state at $\alpha = \alpha_1$, $[AX] = [AX]_1$. This state is obviously unstable and $[AX]$ either jumps to the upper or the lower stable solution. A jump to the lower solution means an increase in $[AX]$ which in turn causes an increase in α (Fig. 2b). Thus, r_R^* inflates until no intersection of r_R^* , r_C^* at the lower branch of r_R^* is possible and $[AX]$ jumps at α_2 along ① to the upper intersection; the reaction ignites.

Now $[AX]$ is in the region of decreasing α -values (Fig. 2b), r_R^* deflates until no intersection at the upper branch of r_R^* is possible, jump ② takes place at α_3 and the oscillation starts again. Thus, $[AX]$ and α form the limit cycle which is plotted in Fig. 2b and the total reaction rate r_A changes with time as plotted in Fig. 2c.

Fig. 3 shows a number of examples for oscillations obtained

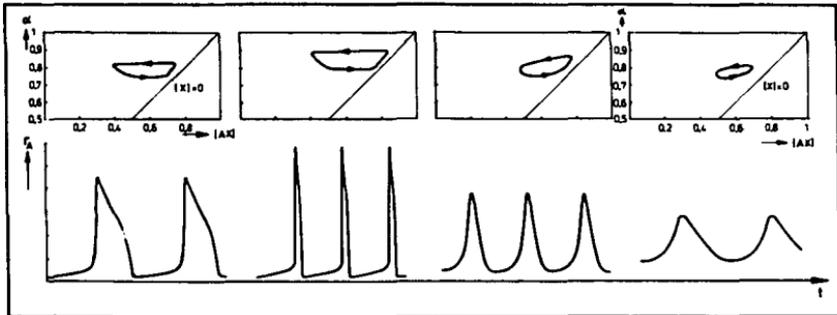


Fig. 3: Calculated oscillations (equ. (10), (11))

by digital simulation of model equs. (10) and (11) with different parameter values.

Application to the CO-oxidation on platinum

The best studied example of kinetic instabilities in heterogeneous reactions is the oxidation of CO on platinum. *Pieguith*

[2;4] investigated rate multiplicity and oscillations using single catalyst pellets in a differential reactor at temperatures above 170°C, *Jakubith* [3;5] made similar studies on Pt-gauze in a loop reactor at temperatures below 150°C. The measured reaction rate at lower temperatures on Pt-gauze was similar to the one given in Fig. 1b, whereas at higher temperatures on single pellets a rate dependency as in Fig. 1a was observed. Oscillations which have been measured on single pellets were of the types shown in Fig. 3 and occurred at CO-concentrations *above* the rate maximum whereas oscillations in the loop reactor were observed at concentrations *below* the rate maximum.

Applying the rate model discussed before, CO would correspond to A, O₂ to B and CO₂ to C. Since it is generally assumed that at least two different types of chemisorbed oxygen with considerably different reactivity towards CO are present on Pt, D could also be considered to be oxygen, with DX a chemisorbed form of oxygen which does not take part in the reaction.

There are some open questions concerning the influence of film and pore diffusion on the measured reaction rates for single pellets, so a quantitative comparison will only be shown for experimental results obtained in a loop reactor and given in [3]. Since the recirculation ratio in the loop reactor was high the reactor can be treated as a CSTR. So only a mass balance for CO=A has to be added if we attempt to model this system with the kinetic equations given before.*)

The mass balance for CO is

$$\frac{d[A]}{dt} = \frac{q}{V}(c_0 - [A]) + \{k_1[AX] - k_1[A][X]\}SC, \quad (15)$$

where c_0 is the feed concentration and SC is the specific surface capacity of the platinum gauze with respect to the reactor volume. Values of the kinetic parameters used in the simulation are given in Table I.

*) It will be assumed that O₂=B=D is present in great excess so that its concentration can be considered constant.

Table I

$k_1 = 1296 \text{ 1/s}$ $k_2 = 0.125 \text{ 1/s}$ $k_4[0] = 0.3125 \text{ 1/s}$ $k_4 = 0.0208 \text{ 1/s}$
 $k_3[0] = 170.7 \text{ 1/s}$ $SC = 0.00236$ $\frac{q}{V} = 1/60 \text{ 1/s}$

In Fig. 4a the steady state reaction rate r over $[CO]$ is plotted.

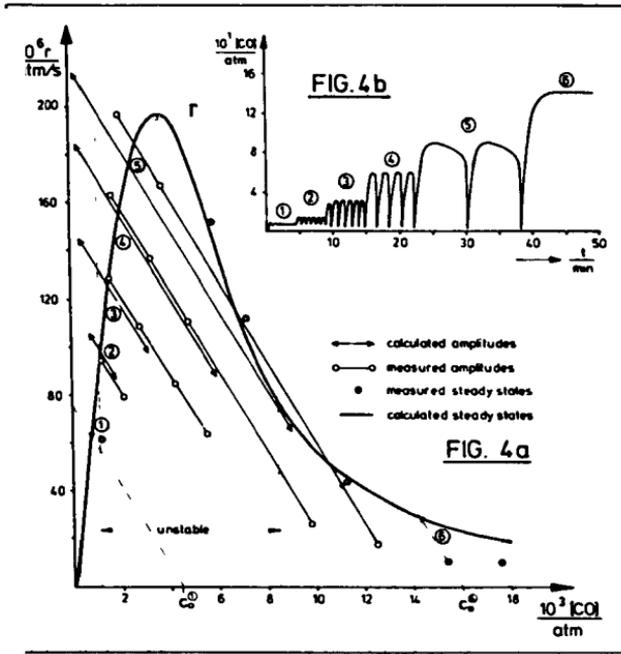


Fig. 4: Steady state behaviour and oscillations in the loop reactor. Comparison of experimental results and simulation at 123°C.

Following the fundamental treatment of Matsuura and Kato [6] the steady state, depending upon the feed concentration c_0 , can easily be constructed by means of the transport line through $[CO] = c_0$ with slope $(-q/V)$.

Increasing c_0 from 0 leads to successive steady states - e.g. no. ① - until the stability limit (obtained by stability

analysis of the linearized system equs.) is reached. If c_0 is increased further, oscillations develop - no. ② / ⑤ - as can be seen in Fig. 4b. The oscillatory instability prevails throughout the region of high reaction rates until new stable steady states - no. ⑥ - are obtained.

Steady state dependency, stability range and periods of oscillations are in accordance with experimental findings. However, in the experiments no smooth transition from the region of small amplitudes to that of high amplitudes took place. A stochastic succession of small, high frequency oscillations followed by a few low frequency overshoots was observed instead.

Conclusions

The results throw a new light upon the problem of multiple steady states in fixed bed reactors. Using the model proposed it can be shown that in case of the CO-oxydation on Pt, multiple solutions are possible in the isothermal fixed bed reactor [9]. This instability is of course amplified by thermal effects during nonisothermal operation. Current models, based upon the assumption of merely thermal instabilities, are therefore not able to predict the hysteresis between ignition and blow out of the reaction with sufficient accuracy. This has been demonstrated by Hlavacek and Votruba [10] in their comparison of experiments with various models.

The results may also lead to a better understanding of the phenomenon of flickering of catalytic wires. It was shown by Ray et.al. [11] that thermal effects alone are not responsible for this kind of instability.

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