

Nu_{Ls} = liquid-to-particles, defined
 R = global rate of reaction, kmol/(kg)(s)
 r_p = radius of spherical particle, m
 V_{mn}, V'_{mn} = parameters defined by Eqs. 8 and 9
 x, y, z = rectangular coordinates
 X, Y, Z = dimensionless spherical coordinates

Greek Letters

δ_m = constant defined by Eq. 7
 ϵ_p = porosity of particles
 λ_m, λ_n = constants defined by Eqs. 5 and 6
 η_o = overall effectiveness factor calculated by the cubical model, Eq. 2 and similar expressions
 η_{om} = overall effectiveness factor calculated from Eq. 14
 η_{os} = overall effectiveness factor calculated by the weighting-factor model (Eq. 10)
 η_L = conventional effectiveness factor based upon ϕ_s and given by Eq. 13 for a spherical catalyst particle

ρ_p = density of particle, kg/m³
 ϕ = Thiele modulus for cubical particle
 ϕ_s = Thiele modulus for spherical particle, defined by Eq. 12
 ϕ'_s = modified Thiele modulus for spherical particle, defined by Eq. 12a

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Two-Step Catalytic Reactions: Pitfalls in the Prediction of Transient Behavior by Global Kinetics

MASSIMO MORBIDELLI,
 GIUSEPPE CITTERIO
 and SERGIO CARRÀ

Dipartimento di Chimica Fisica Applicata del Politecnico
 Piazza Leonardo da Vinci
 Milano, Italy

INTRODUCTION

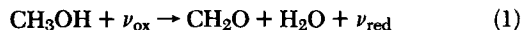
In heterogeneous catalysis chemical reactions occur through a sequence of elementary steps which involve highly reactive intermediates called active centers. The complete description of every single step of the sequence usually leads to rather complicated rate expressions. The most important general technique applied to simplify such expressions is the steady-state approximation of the active sites, which allows to formulate a global rate expression. Moreover, other approximations such as the rate-determining step and the most abundant surface intermediate (which replaces the first one when the elementary reactions of the sequence are irreversible) can be introduced to further simplify the global rate expression by decreasing the number of the involved adjustable parameters (Boudart, 1968).

The steady-state approximation is obviously correctly applicable only to the reacting system in stationary conditions, while the transient requires to describe the entire sequence of elementary steps. For example, this is done in the interpretation of oscillations in surface catalyzed reactions (Sheintuch and Schmitz, 1977), and in the discrimination among rival kinetic models performed exploiting the superior information content of transient experimental data (Bennet, 1976).

This paper points out the pitfalls associated with the application of rate expressions obtained using the steady-state approximation for the description of the transient behavior of a chemical reactor, which is of crucial importance to the definition of the reactor

steady-state stability character. Some of the parameters which characterize the dynamic behavior of the reactor do not affect its steady-state performance. Thus, global rate expressions calibrated on steady-state experiments do not allow the correct design of chemical reactors, which includes the definition of their steady-states stability character.

We will focus here on the redox mechanism which is a quite common example for two-step reactions (Boudart, 1972; Carrà and Forzatti, 1977). We consider the oxidation of methanol to formaldehyde over catalysts of iron molybdate, recently investigated by Santacesaria et al. (1981):



The reaction rates of the two elementary steps are

$$f_1 = k_1 C_M \nu_{\text{ox}} \quad (3)$$

$$f_2 = k_2 C_O^{1/2} \nu_{\text{red}} \quad (4)$$

Recalling that $\nu_{\text{red}} = 1 - \nu_{\text{ox}}$ and using the active sites steady state approximation, from Eqs. 3 and 4 it follows

$$\nu_{\text{ox}} = k_2 C_O^{1/2} / (k_1 C_M + k_2 C_O^{1/2}) \quad (5)$$

Substituting Eq. 5 in Eq. 3, the global rate expression of the process can be derived

$$f = k_1 C_M k_2 C_O^{1/2} / (k_1 C_M + k_2 C_O^{1/2}) \quad (6)$$

Correspondence concerning this paper should be addressed to S. Carrà.

The experimental verification of Eq. 6 and the values of the involved kinetic parameters, where for sake of simplicity the inhibiting effect of water has been neglected, are reported by Santacesaria et al. (1981).

It is worthwhile mentioning also the Langmuir-Hinshelwood kinetics where, according to the rate determining step approximation, all the adsorption and desorption processes are assumed to be at equilibrium conditions. The transient behavior of a catalyst particle where a reaction of this type occurs has been studied by Pereira and Varma (1979) and Elnashaie and Cresswell (1973, 1974). The latter showed that, if the reactant adsorption rate is not assumed instantaneous, both the particle steady state and its stability character can be completely different. Thus in this case, the rate determining step approximation can be verified on the basis of steady states kinetic experiments.

TRANSIENT MODELS OF A CSTR

With illustrative purposes, let us consider a CSTR where the methanol oxidation reaction is performed. The following assumptions are introduced in order to simplify the mathematical treatment:

- Mixture density and specific heat are constant with temperature and composition.
- Inter- and intra-particle mass and heat resistances are negligible.

These assumptions lead to a lumped parameter model, and do not alter the significance of the conclusions of this work.

In the first model the steady state approximations of active sites is used. Thus, using the global rate expression (6) the approximate transient material balance in dimensionless form is given by:

$$\dot{V}_0 = (1 - V_0) - \frac{1}{2} \chi \phi r \quad (7)$$

$$\dot{V}_M = (1 - V_M) - \phi r \quad (8)$$

$$\dot{u} = (1 - u) + \beta \phi r - \delta(u - u_a) \quad (9)$$

with ICs: $V_0 = V_0^{\text{in}}$; $V_M = V_M^{\text{in}}$ and $u = u^{\text{in}}$ at $\theta = 0$; where

$$V_0 = C_0/C_0^0; \quad V_M = C_M/C_M^0; \quad u = T/T^0; \quad \theta = tQ/V_g$$

$$\phi = V_g f^0/QC_M^0; \quad \chi = C_M^0/C_0^0; \quad \beta = (-\Delta H)C_M^0/\rho C_p T^0 \quad (10)$$

$$\delta = UA/Q\rho C_p; \quad \omega = f_2^0/f_1^0 = k_2^0 C_0^{1/2}/(k_1^0 C_M^0);$$

$$\gamma_1 = E_1/RT^0; \quad \gamma_2 = E_2/RT^0; \quad g_1 = \exp\{\gamma_1(1 - 1/u)\};$$

$$g_2 = \exp\{\gamma_2(1 - 1/u)\}; \quad r = f/f^0 = g_1 g_2 V_M V_0^{1/2} (1 + \omega)/(g_1 V_M + g_2 V_0^{1/2}) \quad (11)$$

and the dot indicates the derivative with respect to θ . In the second model, both the elementary reaction steps (1) and (2), and their reaction rates (3) and (4), are taken into account. This is then the complete model, and it includes also the balance of the oxidized active sites ν_{ox} :

$$\dot{V}_0 = (1 - V_0) - \frac{1}{2} \phi_1 \omega \chi r_2 \quad (12)$$

$$\dot{V}_M = (1 - V_M) - \phi_1 r_1 \quad (13)$$

$$\dot{u} = (1 - u) + \phi_1 \beta [\alpha r_1 + (1 - \alpha) r_2 \omega] - \delta(u - u_a) \quad (14)$$

$$\dot{\nu}_{\text{ox}} = \phi_1 \sigma (\omega r_2 - r_1) \quad (15)$$

with ICs: $V_0 = V_0^{\text{in}}$; $V_M = V_M^{\text{in}}$; $u = u^{\text{in}}$ and $\nu_{\text{ox}} = \nu_{\text{ox}}^{\text{in}}$ at $\theta = 0$; where the new parameters are defined as follows:

$$\phi_1 = V_g f_1^0/QC_M^0; \quad \sigma = C_M^0/\nu_{\text{tot}}; \quad \alpha = \Delta H_1/(\Delta H_1 + \Delta H_2) \quad (16)$$

$$r_1 = f_1/f_1^0 = g_1 V_M \nu_{\text{ox}}; \quad r_2 = f_2/f_2^0 = g_2 V_0^{1/2} (1 - \nu_{\text{ox}}) \quad (17)$$

It is noticeable that the two models are characterized by the same dimensionless parameters (ϕ and ϕ_1 are equivalent, since they

differ only for the reference reaction rate) with the only exception of $\nu_{\text{ox}}^{\text{in}}$, ν_{tot} and α which appear only in the complete one. The first two parameters refer to the characterization of the catalyst surface from the active sites point of view, while the third one indicates the contribution of the first reaction step (1), to the global heat of reaction $\Delta H = (\Delta H_1 + \Delta H_2)$.

At steady state, all the time derivatives vanish and from Eq. 15 it follows

$$r_1 = \omega r_2 \quad (18)$$

By inspection of Eqs. 14 and 15 it can be readily seen that the two parameters σ and α do not affect the system steady state, which, as expected, is the same for the two models since $\phi_1 r_1 = \phi r$ as it can be shown using Eqs. 11 and 17 and evaluating ν_{ox} from Eq. 18. However, the transient behavior predicted by the two models is different, and therefore the stability character of the steady state can be different. This fact is quite evident since the two parameters σ and α , which do not appear in the approximate model, do actually affect the solution of the complete model.

From Eq. 15 it follows that as $(\phi_1 \sigma) \rightarrow \infty$, $(\omega r_2 - r_1) \rightarrow 0$, since ν_{ox} must be finite, and therefore the two models give the same results also with respect to the transient behavior. This fact is physically reasonable since $(\phi_1 \sigma)$ represents the ratio between the moles of active sites involved in the first reaction ($f_1^0 V_g/Q$) and the total number of available active sites, ν_{tot} . Therefore $(\phi_1 \sigma) \rightarrow \infty$, means that the active sites are highly reactive and they must all collaborate to carry on the reaction, and therefore their concentration closely approaches steady state conditions. In other words, the storage capacity of the catalytic surface for intermediate reactants becomes too small to affect the dynamics.

STABILITY AND TRANSIENT BEHAVIOR

Since the two models are complicated and include a large number of physicochemical parameters, it is not possible to investigate all aspects of steady state and dynamic behavior. Instead, few cases are considered which reveal some interesting differences between the two models in describing the steady states stability and the transient behavior of the reactor under examination.

The two models have been solved by means of the Gear (1975) integration method and using the parameter values reported in Table 1, which have been calculated according to Santacesaria et al. (1981). The problem is obviously the evaluation of σ and α , that is of the total active sites concentration ν_{tot} and the enthalpy change associated with reaction 1 (or 2, since their sum is known). These values have not been reported in the above mentioned paper, and in general they can not be evaluated from experimental data taken under steady state conditions, since, as previously noticed, they do not affect the reactor steady state. However, suitable procedures can be applied in order to obtain at least an approximate estimation of such values.

According to Maatman (1976) an upper limit of 10^{15} sites per catalyst cm^2 (i.e., $\nu_{\text{tot}} = 2.4 \cdot 10^{-4} \text{ mol/cm}^3$, $\sigma = 0.039$) can be estimated assuming that each site occupies 10 \AA^2 on the catalyst surface.

As a first approximation the value of α can be estimated assuming that during reaction 2 MoO_2 is oxidized all the way to

TABLE 1. VALUES OF THE DIMENSIONLESS PARAMETERS USED IN THE NUMERICAL CALCULATIONS

Adiab.	Nonadiab.	Adiab.	Nonadiab.
$\beta = 3.194$	4.0596	$\gamma_1 = 23.19$	25.64
$\delta = 0.0$	4.640	$\gamma_2 = 15.20$	16.81
$\phi = 2.37 \cdot 10^{-4}$	0.025	$u_a = -$	1.00
$\phi_1 = 8.81 \cdot 10^{-4}$	0.052	$(+)V_M^s = 0.652$	0.4069
$\chi = 5.0$	3.350	$(+)V_0^s = 0.130$	$6.68 \cdot 10^{-3}$
$\omega = 0.3671$	0.925	$(+)u^s = 2.111$	1.427

(+) In this case three steady states are present; the only high-conversion one is reported.

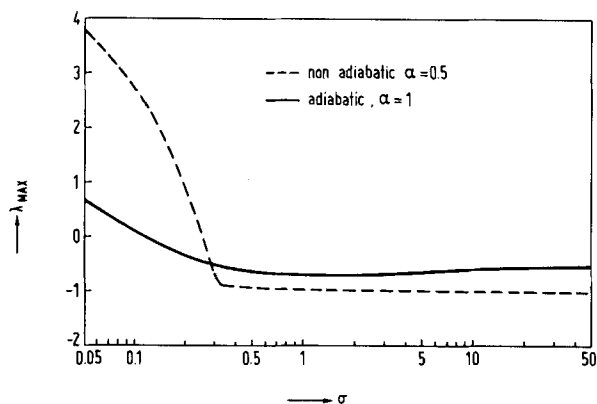


Figure 1. Largest real part of the eigenvalues, λ_{MAX} as a function of σ , relative to the high-conversion steady state reported in Table 1.

MoO₃. The enthalpy change of this process is about $\Delta H_2 = -37.6$ kcal/mol. Since $\Delta H = -36.8$ kcal/mol, it follows $\Delta H_1 = 0.8$ kcal/mol, and then $\alpha = -0.022$.

Since these values can only be regarded as rough approximations, in the following we will examine a wide range of values for σ and α , centered on the previously obtained results. With reference to Table 1, the steady states for the reacting systems have been calculated for two situations: an adiabatic reactor and a reactor with heat exchange (in particular, this is the one used by Santacesaria et al., 1981). In both cases three steady states were found, and their local stability were then analyzed through the first Liapunov method. Let us focus on the high conversion steady state: its stability character depends on the values of σ and α for the complete model, while it is always asymptotically stable for the approximate model.

In Figure 1 the value of the largest real part of the eigenvalues, obtained through linearization around the high-conversion steady state, is shown as a function of σ , for both the adiabatic and the non-adiabatic cases. Note that using the approximate model, independently of the values of σ and α , $\lambda_{MAX} = -0.54$ and -1 for the two cases, respectively. As expected, from Figure 1 it appears that for increasing values of $\phi_1\sigma$, the ϵ_{MAX} value relative to the complete model approaches the one given by the approximate model. However, for small values of $\phi_1\sigma$ the λ_{MAX} value is positive, so indicating that the high-conversion steady state is unstable. Similarly, the effect of the heat of reaction parameter, α has been investigated in Figure 2. It appears that the value of λ_{MAX} can turn from negative to positive for increasing values of α , with all the other parameters constant. It is then possible to conclude that the

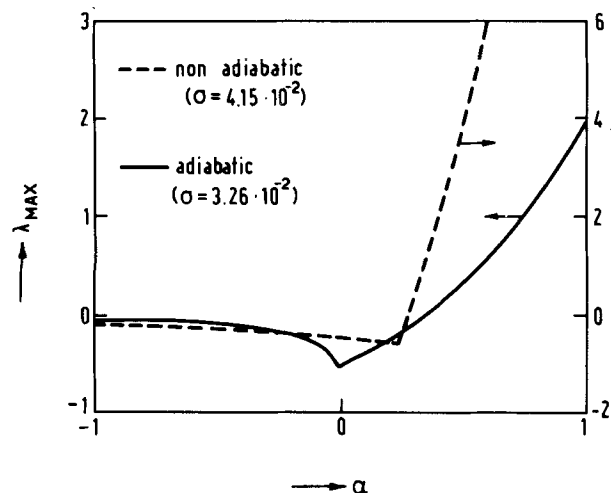


Figure 2. Largest real part of the eigenvalues, λ_{MAX} as a function of α , relative to the high-conversion steady state reported in Table 1.

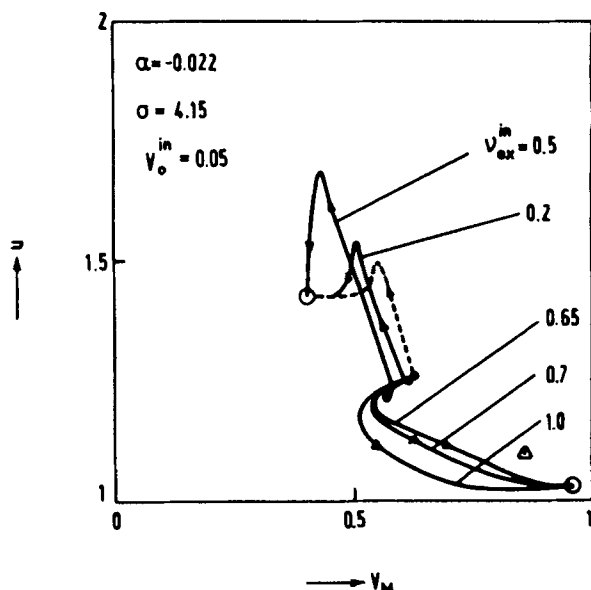


Figure 3. Trajectories in the $(u - V_M)$ plane of the CSTR transient behavior calculated with the complete (—) and the approximate (---) model (● stable steady state; △ unstable steady state; ● initial condition).

stability character of the steady state depends on the values of σ and α , which do not even appear in the approximate model, which is then inadequate for such analysis.

It is noticeable that in the case of an homogeneous adiabatic CSTR with three steady states, the high-conversion one can be proved to be asymptotically stable for all type of rate expressions (Varma and Aris, 1977). Such conclusion can not be extended to catalytic reactions, whose global rate expressions are derived applying the steady state approximation to a sequence of elementary reaction steps.

Another consequence of the different dynamic behavior described by the two models is that, for a given set of initial conditions, a different steady state can be approached using one model or the other. Particularly significant is the role played in this case by the initial condition of the catalytic surface, described by ν_{ox}^{in} . Again,

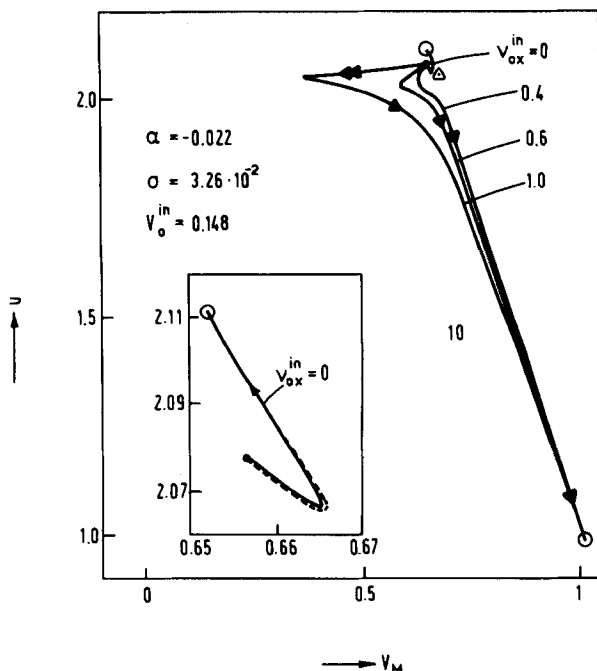


Figure 4. Trajectories in the $(u - V_M)$ plane of the CSTR transient behavior calculated with the complete (—) and the approximate (---) model (● stable steady state; △ unstable steady state; ● initial condition).

this variable does not appear in the approximate model, while it largely affects the results of the complete model. This can be seen from Figures 3 and 4, where the projection of the phase space on the $(u - V_M)$ plane is shown for a non-adiabatic and an adiabatic CSTR, respectively. In it, for a given set of the dimensionless parameters reported in Table 1 and of the initial conditions V_0^{in} , V_M^{in} and u^{in} , the trajectories obtained using the complete model with various values of $\nu_{\text{ox}}^{\text{in}}$ are shown. The trajectory relative to the approximate model is represented by the hatched curve. It is apparent that depending on the value of $\nu_{\text{ox}}^{\text{in}}$, with all the other quantities fixed, the system reaches either the low-conversion steady state (for large $\nu_{\text{ox}}^{\text{in}}$) or the high-conversion one (for small $\nu_{\text{ox}}^{\text{in}}$). In the particular case under examination the separation value is about $\nu_{\text{ox}}^{\text{in}} = 0.07$ and 0.62 for the adiabatic and the non-adiabatic CSTR, respectively. This shows the influence of the catalytic surface pretreatment on the dynamic behavior of the reactor. This fact has been already recognized in catalysis, for example in the case of CO oxidation over platinum (cf, Cutlip, 1979), where a previous exposure to CO leads to the low steady state whereas a previous exposure to O₂ leads to the high steady state.

CONCLUSIONS

It can then be concluded that the application of the steady state approximation to a sequence of elementary reaction steps can lead to serious pitfalls in the definition of the stability character of the system steady state. In particular, the characteristics of the catalytic surface (i.e., σ and $\nu_{\text{ox}}^{\text{in}}$) and the contribution to the heat of reaction of the single elementary step (i.e., α), which do not appear in the approximate model, are instead of crucial importance in the definition of the system transient behavior. Therefore, rate expressions derived on the basis of experimental steady state data can be used only to determine the number and values of a catalytic reactor steady states, but not to inquire on their stability character or on the start-up policy of the reactor itself. In order to evaluate all the parameters of the complete model it is then necessary to consider transient experimental data, since the available procedures for the estimation of σ and α are not fully reliable.

It is worthwhile pointing out that the results reported above refer to the case where the intrinsic time constants of heat and mass transport are equal, i.e., Lewis number equal to one. Besides homogeneous reactors, such values, or even smaller, can be encountered in heterogeneous systems also (Sheintich and Schmitz, 1977).

NOTATION

A	= heat transfer surface area for the reactor
C	= concentration
C_p	= specific heat
E_1, E_2	= activation energy of reactions 1 and 2, respectively
f_1, f_2, f	= reaction rate per unit gaseous volume, given by Eqs. 3, 4 and 6
k_1, k_2	= rate constant of reactions 1 and 2, respectively

Q	= volumetric flowrate
R	= gas constant
T, T_a	= temperature of the reacting mixture and the cooling medium, respectively
t	= time
U	= overall heat transfer coefficient
V_g	= volume of the gaseous reacting mixture

Greek Letters

α	= $\Delta H_1 / (\Delta H_1 + \Delta H_2)$
$\Delta H_1, \Delta H_2$	= heat of reactions 1 and 2
ΔH	= $\Delta H_1 + \Delta H_2$
λ_{MAX}	= maximum real part of the eigenvalues relative to the model linearized around the steady state
$\nu_{\text{ox}}, \nu_{\text{red}}$	= fraction of active sites in the oxidized and reduced state, respectively
ν_{tot}	= total active sites concentration, mol/cm ³ of gaseous phase
ρ	= density of reacting mixture
σ	= C_M^0 / ν_{tot}

Subscripts

in	= initial condition
M	= methanol
O	= oxygen
o	= feed

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