

# Surface Reaction Kinetics by R. K. Herz <herz@ucsd.edu>

## Problem Statement

We start with a reaction mechanism consisting of a list of stoichiometric equations of elementary steps. In this discussion, the list of elementary steps sum to one independent reaction pathway which is catalyzed by the surface of a solid catalyst. From the list of elementary steps, we want to derive equations that will allow us to predict the course of the reaction as it occurs in a reactor. By "predict the course" we mean predict fluid-phase composition vs. time and/or position (and temperature if non isothermal). The types of reactors we are interested in include: ideal batch (dynamic), ideal CSTR (steady state and dynamic) and ideal PFR (steady state and dynamic).

Mechanisms should be developed using all the knowledge about a reaction, and similar reactions, that is available, including experimental data on simplified subsets of the species.

Usually, the ability of a mechanism to predict the course of a reaction is in doubt. We will want to compare the predictions of several alternative mechanisms, and/or the predictions of one mechanism for which several different combinations of simplifying assumptions have been made, to the experimental data. The model that fits the data best might then be put to further experimental tests or, if its predictions are satisfactory, used to design a new reactor or process.

Below, we discuss the two main types of simplifying assumptions or approximations that can be applied: the "steady state approximation" and the "partial equilibrium approximation". Use of these approximations simplifies the equations that must be solved. Note that neither of these approximations must be made, however, they can often be justified physically under specified ranges of conditions. When the approximations are justified but are not made in a numerical model, the solution of the numerical model may be difficult, e.g., stiff differential equations may result.

## Terminology

Any term has several alternatives and you should be able to relate them to each other. The versions used by Michel Boudart in his book "Kinetics of Chemical Processes" are used in these notes.

"Steady state approximation" will be abbreviated here as "SSA".

The following words may be used instead of "steady state": "stationary state", "quasi steady state", "pseudo steady state", "quasi static".

The word "assumption" may be used instead of "approximation".

"Partial equilibrium approximation" will be abbreviated here as "PEA".

The following words may be used instead of "partial equilibrium": "quasi equilibrium", "pseudo equilibrium", or simply "equilibrium".

The word "assumption" may be used instead of "approximation".

"Rate determining step" will be abbreviated here as "RDS".

Alternatives are "rate limiting step" and "rate controlling step".

"Langmuir-Hinshelwood" kinetics and rate equations.

Also called "Hougen-Watson" kinetics and rate equations. These terms are used for reactions catalyzed by solid surfaces. When you see one of these terms applied to a rate equation, it probably means that the rate equation is based on a proposed reaction mechanism, as opposed to being just a completely empirical correlation of experimental data like a power-law rate equation.

Often you will see reference to a "Langmuir-Hinshelwood reaction". Sometimes this term is used loosely to label any mechanism that occurs on a catalyst surface. Other times it is used to specify an elementary reaction step that happens between two adsorbed species, rather than an "Eley-Rideal" reaction step between an adsorbed species and a fluid-phase species.

Irving Langmuir won a Nobel Prize for his pioneering work that put surface chemistry on a sound fundamental basis. Cyril Hinshelwood ["The Kinetics of Chemical Change", Clarendon Press, Oxford (1940)] derived rate equations for a variety of mechanisms based on Langmuir's work. Olaf Hougen and K. Watson [Indus. & Eng.Chem., vol. 35, pp. 529-520 (1943)] extended the development of Hinshelwood.

### General Observations

The SSA and the PEA are different from each other. An SSA is applied to a specified species. A PEA is applied to a specified elementary step. To a given mechanism, one approximation may be applied, or the other may be applied, or both may be applied. Each of these options are shown below.

The SSA can be applied to reactions under dynamic conditions. A steady-state reactor is at steady state by specification, not by approximation. Most kinetics texts automatically consider batch reactors, which operate under dynamic conditions, when discussing approximations (and sometimes don't explicitly state they are considering a batch reactor!). These texts often derive a single overall rate equation that gives the value of the net overall reaction rate as a function of fluid composition and temperature. Of course, an overall rate equation derived using a batch reactor and applying the SSA does not preclude its use in a steady-state CSTR or PFR, since the SSA is not violated. However, as chemical engineers, we know that there are other types of reactors and know to be careful to specify what we are using.

Application of either the SSA or the PEA reduces the number of equations and simplifies the equations used to predict the course of a reaction in a reactor. The cost of this simplification is that the resulting equations only apply to the range of conditions under which the approximations can be justified. To achieve the greatest simplifications, apply the SSA to all surface species and apply the PEA to all elementary steps except one, the rate determining step.

When applied to a batch reactor (dynamic), the SSA and the PEA reduce the number of ordinary differential equations that must be integrated to predict the course of the reaction.

When applied to a steady-state CSTR, the PEA simplifies the algebra required (no differential equations for a steady-state CSTR). A PEA may be required in order to simplify the algebra such that a single rate equation can be obtained (by average mathematicians or impatient kineticists, at least).

For a mechanism with  $n > 1$  steps, a PEA can be applied to from one to up to  $(n - 1)$  of the steps. If a PEA is applied to  $(n - 1)$  steps, the remaining step is called the "rate determining step" (RDS). If both the forward and reverse rate constants of any of the steps in partial equilibrium were to be increased and kept in the same ratio, the overall reaction rate would not change. However, if the forward and reverse rate constants of the RDS were to be increased and kept in the same ratio, the reaction rate would increase.

You may find a mechanism where one or more steps are labeled "fast" and are shown with a single left-to-right arrow, which implies that they are far from equilibrium under all conditions considered. PEAs are not applied to such steps and these steps are not RDS's.

### Development of Equations

First make sure you identify the type of reactor you are considering, sketch and label the sketch, and identify the control volume over which balance equations are written. List major assumptions, e.g., isothermal conditions, etc.

Here, we will assume that no catalyst deactivation occurs on the time scale we are considering. Therefore, a "site balance" can be written that expresses that the sum of all of the surface species is constant and equal to a total number of concentration of active surface sites. If there are different types of surface sites (not different species on one type of site) present, then a site balance is written for each type of site.

The next step is to write balance equations. We consider isothermal systems here so we only have to discuss species balances.

How many species balances do we need to write? You can write one for each species, or you can do a formal stoichiometric analysis to determine the minimum number required, since not all species balances will be independent of each other, or a number in between if you just do an informal stoichiometric analysis by observation.

For a batch reactor we have two options:

- (1) We can write a balance for each chemical species present, including surface species. Some stoichiometric analysis and reduction of the number of equations may be performed by observation. For example, by eliminating the balance for species  $B_i$  if the only reaction in which it is formed is also the only reaction in which species  $A_j$  is consumed.
- (2) We can perform an analysis in order to determine the minimum number of species balances that have to be written. In this option, treat the stoichiometric equations of the elementary steps in the same way we normally treat the stoichiometric equations of reaction pathways when designing a reactor starting with reaction pathways rather than elementary steps. By identifying the chemical elements, chemical species including surface species, and elementary steps (in place of reaction pathways), we can identify a set of independent stoichiometric equations and write a "stoichiometric table" that relates the number of moles of each species present to the starting composition and the "stoichiometric extent" or "extent of reaction" variable(s). After applying any simplifying approximations to the species balances, and then substituting the relationships in the stoichiometric table into the independent species balances, we end up with one differential equation for each extent variable.

For a CSTR or PFR under dynamic conditions, species balances also can be written for surface species as well as fluid-phase species. However, since the stable species flow in and out of the reactor and the surface species

do not, it is not possible to define extents of reaction as in method (2) for batch reactors. Some stoichiometric analysis and reduction of the number of equations may be performed by observation. For example, by eliminating the species balance for species  $B_i$  if the only reaction in which it is formed is also the only reaction in which species  $A_j$  is consumed.

For a CSTR or PFR at steady state, species balances can be written on the stable species that flow into and out of the reactor. Since we are considering a system here with only one reaction pathway and one independent stoichiometric equation, a species balance only needs to be written on one stable species. Whereas species balances can be written on the surface species, these balances only state that the net rate of formation of each surface species is zero, thus, they are not usually written out.

After the initial species balances are written, the equations either can be solved as formulated or simplifying assumptions - SSA and/or PEA - can be made in order to simplify the solution. SSAs can be made for species in dynamic systems; systems specified to be at steady-state require no SSA.

### Notes on the examples

The example below has derivations for a mechanism discussed by Michel Boudart in his book "Kinetics of Chemical Processes." Equations are set up for the following cases of this reaction in a batch reactor: no approximations applied, SSA applied, PEA applied, both SSA and PEA applied. Although application of the SSA and PEA are given for a simple two-step example, the same principles and procedures apply to more complicated reaction mechanisms.

One of the reasons I like Boudart's book is that it tries to show the similarities between the kinetics of reaction mechanisms occurring on catalyst surfaces with those occurring homogeneously. In doing research on how gas phase kineticists use the SSA and PEA, I consulted Forman William's book, "Combustion Theory" (2nd ed., Addison-Wesley, 1985, UCSD S&E Library, QD516.W56). See especially Appendix B, "Review of Chemical Kinetics."

The equations in the example below can also be used for homogeneous catalysis. In such a case, the units of the X species are  $\text{mol m}^{-3}$  of fluid and the ratio  $(W_{\text{cat}}/V)$  becomes  $(V/V) = 1$ .

The second example in a separate set of notes applies these simplifying techniques to the ammonia synthesis reaction mechanism presented by Ertl in "Elementary Steps in Ammonia Synthesis," pp. 109-132 in "Catalytic Ammonia Synthesis : Fundamentals and Practice," edited by J.R. Jennings. New York : Plenum Press (1991).

If you use this course as part of an "area" for an oral exam, I expect you to be able to answer some relatively simple questions about surface structure and analysis and to be able to derive equations for some relatively simple surface processes. For example, you should be able to state the assumptions for and derive equations for the examples discussed in Chapter 10 (3rd ed.) of H. Scott Fogler's "Elements of Chemical Reaction Engineering" (Prentice-Hall, 1999, UCSD S&E Library, TP157.F65): Langmuir adsorption of a single species, dissociative adsorption of a single species, competitive adsorption of two species on a single type of site, and some simple reactions. Although you may have also studied these simple examples in an undergraduate course, as a graduate student I expect that you should be able to understand them now.

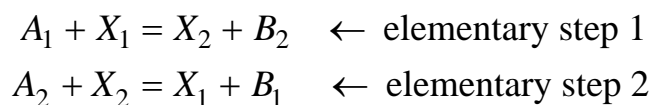
Note that all of the derivations in Fogler, Boudart and in class specify a simple surface. That is, we have specified the assumptions that apply to the Langmuir isotherm: the surface is considered as an fixed array of identical sites that have constant properties, the adsorbed species are distributed randomly over the surface, and the energy of interaction between adsorbed species and sites are independent of coverage. These assumptions

probably don't describe any real surface, thus all of the mechanisms and rate equations are simplified approximations. They are useful because they often are able to do a good job at fitting data.

Some of the most exciting work in surface reactions currently is work on surfaces and reactions that don't obey these assumptions. Much of this work has been done in Germany by Gerhard Ertl and colleagues. At the end of these notes, I have listed references to some of this work. Many of the papers have neat photos or other graphics, so they are definitely worth looking at if you are interested in surface processes.

### Example - General 2-Step Mechanism

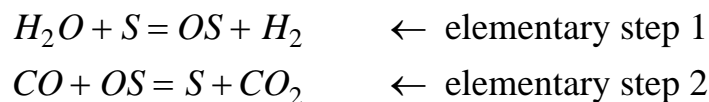
Michel Boudart, in his book "Kinetics of Chemical Processes" (Prentice-Hall, 1968, UCSD S&E Library QD501.B7818), discusses the following generalized two-step mechanism for a catalytic reaction:



where the subscripts are merely indexes and are not chemical notation that represent number of atoms. The X's are catalytic species, in either the fluid phase or over the surface of a solid catalyst, and the A's and B's are fluid-phase species. For an alternate case where one of the A or B species is not present, replace its concentrations in the rate expressions below by 1, not 0.

Boudart also refers to this type of mechanism as a "closed" catalytic mechanism, and refers to the X's as "active centers" and "reactive intermediates." The SSA and PEA can also be applied to "open" mechanisms where some of the active centers undergo net creation or destruction

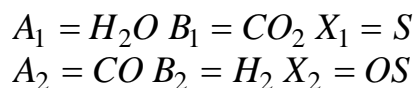
An example of a two-step catalytic reaction of this type given by Boudart is the solid-surface-catalyzed "CO shift" reaction, or "water-gas shift" reaction:



where S is an empty surface "site" and OS is an oxygen atom adsorbed over a surface site.

In these notes, we consider the catalytic species X to be species over the surface of a solid catalyst. The equations developed here can also be used for homogeneous catalysts. In such a case, the units of the X species are mol m<sup>-3</sup> of fluid and the ratio (W<sub>cat</sub>/V) below becomes (V/V) = 1.

The relationships between the two notations are:



Since we want to have equations that describe how the concentrations of the species change with time in a batch reactor, we want to write species balances. How many balances do we need to write for these six species? Since we have two independent elementary steps, we will only have to write two independent balances. First, let's write a stoichiometric table for the system of elementary steps:

Stoichiometric table:

$$\begin{aligned}
 A_1 &= A_1^0 && - \varepsilon_1 \\
 A_2 &= A_2^0 && - \varepsilon_2 \\
 B_1 &= B_1^0 && + \varepsilon_2 \\
 B_2 &= B_2^0 && + \varepsilon_1 \\
 X_1 &= X_1^0 - \left( \frac{V}{W_{cat}} \right) \varepsilon_1 + \left( \frac{V}{W_{cat}} \right) \varepsilon_2 \\
 X_2 &= X_2^0 + \left( \frac{V}{W_{cat}} \right) \varepsilon_1 - \left( \frac{V}{W_{cat}} \right) \varepsilon_2
 \end{aligned}$$

where  $A_i$  and  $B_i$  ( $\text{mol m}^{-3}$  fluid) are the concentrations of the fluid-phase species,  $X_i$  ( $\text{mol kg}^{-1}$  catalyst) are the concentrations of the surface species, and where  $\varepsilon_1$  and  $\varepsilon_2$  ( $\text{mol m}^{-3}$ ) are the stoichiometric extents of steps 1 and 2, respectively. We see that balances on two species that give independent information about the two extents  $\varepsilon_1$  and  $\varepsilon_2$  are sufficient. For example, the following pairs work:  $A_1$  and  $A_2$ ,  $B_1$  and  $B_2$ ,  $A_1$  and  $B_1$ ,  $A_1$  and  $X_1$ . The pair  $A_1$  and  $B_2$ , and the pair  $X_1$  and  $X_2$  do not work.

Below, we write balances on  $A_1$  and  $X_1$ . Following changes in  $A_1$ , we can get  $\varepsilon_1$ :

$$\varepsilon_1 = (A_1^0 - A_1)$$

Following changes in  $X_1$  and knowing  $\varepsilon_1$ , we can get  $\varepsilon_2$ :

$$\varepsilon_2 = (A_1^0 - A_1) - \left( \frac{W_{cat}}{V} \right) (X_1^0 - X_1)$$

Knowing  $\varepsilon_1$  and  $\varepsilon_2$ , we can compute the concentrations of the other four species using the stoichiometric table.

Without applying the SSA or the PEA, we will have two ODE's to integrate. We could also express the two ODEs to be integrated in terms of concentrations. For example, we can write species balances on  $A_1$  and  $X_1$ :

Balance on species  $A_1$  in a constant volume, isothermal, ideal batch reactor:

$$\frac{dn_{A_1}}{dt} = r_{A_1} W_{cat}$$

where  $n_{A_1}$  (mol) is the number of moles of  $A_1$  in the reactor,  $r_{A_1}$  ( $\text{mol s}^{-1} \text{kg}^{-1}$ ) is the net rate of generation of  $A_1$ , and  $W_{cat}$  (kg) is the mass of solid catalyst in the reactor. Since the reactor has constant volume,  $n_{A_1} = VA_1$ , where  $V$  ( $\text{m}^3$ ) is the volume of the fluid phase in the reactor.

Steps 1 and 2 are elementary reactions. In order to write rate expressions for them, we need to make some simplifying assumptions.

We invoke the assumptions of "Langmuir-Hinshelwood" kinetics:

- uniform surface consisting of a fixed array of identical "sites" with constant properties
- adsorbed species are distributed randomly over the surface, e.g., by rapid surface diffusion
- the energy of interaction between an adsorbed species and the surface remains constant as the surface coverage changes

Note that the above assumptions probably don't hold true for any real surface. Thus, we develop approximate models of real systems rather than completely accurate descriptions. Now we can write rate expressions for the two elementary steps in order to get  $r_{A_1}$  in terms of the species concentrations:

$$\frac{dA_1}{dt} = -k_1 A_1 X_1 \left( \frac{W_{cat}}{V} \right) + k_{-1} X_2 \left( \frac{W_{cat}}{V} \right) B_2$$

where units the units of the rate coefficients are ( $\text{m}^3 \text{s}^{-1} \text{mol}^{-1}$ ). In Boudart's examples, the group  $(W_{cat}/V)$  is not used. To eliminate it for a surface-catalyzed reaction, the surface species concentration  $X_1$  would have to have units (moles adsorbed per volume of fluid) and the rate  $r_{A_1}$  would be per unit volume of fluid. That can be done, and doing it results in a simpler form of the equation, but such units are not practical to work with on a real problem in heterogeneous catalysis, especially if we want to vary the catalyst to fluid volume ratio. In addition, making the group  $(W_{cat}/V)$  explicit will help to justify the SSA below. Many other authors often ignore units but I recommend balancing units, at least at the start of a derivation.

Balance on surface sites  $X_1$ :

$$\frac{dn_{X_1}}{dt} = r_{X_1} W_{cat}$$

$$n_{X_1} = W_{cat} X_1$$

$$\frac{dX_1}{dt} = -k_1 A_1 X_1 + k_{-1} X_2 B_2 + k_2 A_2 X_2 - k_{-2} X_1 B_1$$

In order to integrate the two ODEs, we also need to use the stoichiometric table to express the concentrations of the other four species in terms of  $A_1$  and  $X_1$ :

$$A_2 = A_2^0 - (A_1^0 - A_1) + (X_1^0 - X_1) \left( \frac{W_{cat}}{V} \right)$$

$$B_1 = B_1^0 + (A_1^0 - A_1) - (X_1^0 - X_1) \left( \frac{W_{cat}}{V} \right)$$

$$B_2 = B_2^0 + (A_1^0 - A_1)$$

$$X_2 = X_1^0 + X_2^0 - X_1 = X_{total} - X_1$$

The last relationship uses the fact that the total number of surface sites is assumed to remain constant during reaction:

$$X_1 + X_2 = X_{total} \quad \text{the "site balance"}$$

The symbol L used by Boudart equals  $X_{total}$  here. Finally, we need initial conditions:

$$\text{Initial conditions : } A_1(0) = A_1^0 \quad ; \quad X_1(0) = X_1^0$$

Another way we can express these two ODEs is directly in terms of the extent variables. The shortest path to these equations is to start with balances on either  $A_1$  and  $A_2$  or  $B_1$  and  $B_2$  and then substitute the dependence of the concentrations variables on the extents:

$$\frac{d\varepsilon_1}{dt} = k_1 \left( A_1^0 - \varepsilon_1 \right) \left( X_1^0 \left( \frac{W_{cat}}{V} \right) + \varepsilon_2 - \varepsilon_1 \right) - k_{-1} \left( X_2^0 \left( \frac{W_{cat}}{V} \right) + \varepsilon_1 - \varepsilon_2 \right) \left( B_2^0 + \varepsilon_1 \right)$$

$$\frac{d\varepsilon_2}{dt} = k_2 \left( A_2^0 - \varepsilon_2 \right) \left( X_2^0 \left( \frac{W_{cat}}{V} \right) + \varepsilon_1 - \varepsilon_2 \right) - k_{-2} \left( X_1^0 \left( \frac{W_{cat}}{V} \right) + \varepsilon_2 - \varepsilon_1 \right) \left( B_1^0 + \varepsilon_2 \right)$$

$$\text{Initial conditions : } \varepsilon_1(0) = \varepsilon_2(0) = 0$$

We now have two coupled ODEs to integrate in order to describe how the concentrations in our batch reactor change with time. For one reaction pathway in a batch reactor, we usually expect to see one ODE with one overall rate expression (rate equation, rate law) on the right hand side. What's up? Well, we can get to that one ODE with one overall rate expression, but we have to make some further simplifying assumptions in order to do so.

### Apply the Steady-State Approximation

Steady-state approximations are often applied to reactive intermediates such as free radicals in gas-phase reaction mechanisms. Boudart says the SSA is the most important general technique in applied chemical kinetics. In many cases, the SSA can be applied to surface species.

Steady-state approximations are applied to species. In the reaction considered here, we have to apply the approximation to both surface species, since their concentrations are directly linked:



$$\frac{dX_1}{dt} = -\frac{dX_2}{dt}$$

Divide  $(dX_1/dt)$  by  $(dA_1/dt)(V/W_{cat})$ :

$$\frac{(dX_1/dt)}{(V/W_{cat})(dA_1/dt)} = \frac{-k_1A_1X_1 + k_{-1}X_2B_2 + k_2A_2X_2 - k_{-2}X_1B_1}{-k_1A_1X_1 + k_{-1}X_2B_2}$$

$$\frac{(dX_1/dt)}{(V/W_{cat})(dA_1/dt)} = 1 + \frac{k_2A_2X_2 - k_{-2}X_1B_1}{-k_1A_1X_1 + k_{-1}X_2B_2}$$

If we can show for our system that the following criterion holds:

$$\frac{(dX_1/dt)}{(V/W_{cat})(dA_1/dt)} \ll 1$$

then

$$k_1A_1X_1 - k_{-1}X_2B_2 \approx k_2A_2X_2 - k_{-2}X_1B_1$$

Rearranging the criterion, we see that we need the rate of change in number of moles of surface species to be much less than the rate of change of the number of moles of fluid-phase species:

$$W_{cat}(dX_1/dt) \ll V(dA_1/dt)$$

The "quick" way to apply the SSA is to set the time derivative of the reactive species, in this case the surface species, to zero:

$$0 \approx \frac{dX_1}{dt} = -k_1A_1X_1 + k_{-1}X_2B_2 + k_2A_2X_2 - k_{-2}X_1B_1$$

which results in the same relationship between the surface and fluid-phase species that we obtained above:

$$k_1A_1X_1 - k_{-1}X_2B_2 \approx k_2A_2X_2 - k_{-2}X_1B_1$$

However, be careful and remember that we are saying that the rate of change of the reactive species is small relative to the rate of change of the stable species, not that the rate of change of the reactive species is zero.

Keep in mind that the SSA is an approximation and the predicted course of the reaction will deviate from the result that would be obtained if no approximation were made. In general, if the approximation was justified correctly, the deviations will be significant only at early times and at long time. See the discussion in Boudart and also in Bowen, Acrivos and Oppenheim, Chem. Eng. Sci., vol. 18, pp. 177-188 (1963).

Our criterion for the SSA that

$$W_{cat}(dX_1/dt) \ll V(dA_1/dt)$$

will be true when the total number of moles of surface species or surface sites is much less than the maximum number of moles of fluid-phase species in the reactor. That is, when:

$$W_{cat}X_{tot} \ll V(A_1^0 + A_2^0 + B_1^0 + B_2^0)$$

Another way you will see the SSA justified is through a comparison of time constants or characteristic times of the rates of change of surface and fluid-phase species. Consider our system with all fluid-phase species equal to zero except that the concentration  $A_1$  is at its maximum level, and with  $X_2 = 0$  such that we have a "clean surface" where  $X_1 = X_{tot}$ . The balance for  $A_1$  at early time is:

$$\frac{dA_1}{dt} = -\left(\frac{k_1 W_{cat} X_1}{V}\right)A_1$$

The characteristic time for the initial disappearance of  $A_1$  is

$$\tau_{A_1}(s) = \frac{V}{k_1 W_{cat} X_1}$$

The balance for  $X_1$  at early time is:

$$\frac{dX_1}{dt} = -k_1 A_1 X_1$$

The characteristic time for the initial disappearance of  $X_1$  is

$$\tau_{X_1}(s) = \frac{1}{k_1 A_1}$$

The criterion for the SSA approximation to apply is

$$\tau_{X_1}(s) \ll \tau_{A_1}(s)$$

This means that

$$\frac{1}{k_1 A_1} \ll \frac{V}{k_1 W_{cat} X_1}$$

$$W_{cat} X_1 \ll V A_1$$

Therefore, the time constant criterion is equivalent to the criterion that the total number of moles of surface species or surface sites is much less than the maximum number of moles of fluid-phase species in the reactor.

This example only involves adsorption of one species to form  $X_2$ , where  $X_1$  can be considered a "vacant" or "empty" surface site. In some cases in which there is competitive adsorption of two or more species on the same surface sites, Klein and Schmidt (J.Chem.Phys., 1982, vol. 76, p. 3823) have shown that there may be long transients on the surface due to slow displacement of one surface species by another, so additional criteria may be required for justification of the SSA.

Note that criteria for application of the SSA to homogeneous mechanisms will differ. For homogeneous "closed" mechanisms involving a homogeneous catalyst such as a biological enzyme, the units of  $X$  are ( $\text{mol m}^{-3}$ ) and  $W_{\text{cat}}$  is replaced by  $V$ , with the criterion otherwise remaining the same. For homogeneous "open" mechanisms, there is no limit corresponding to the "site balance" and justifications of the SSA must be based on a comparison of rate coefficients (Boudart, pp. 63-67 of 1991 Butterworth-Heinemann reprint) rather than the "relative capacity" criterion for "closed" mechanisms such as the one in this example.

$$W_{\text{cat}}X_{\text{tot}} \ll V(A_1 + A_2 + B_1 + B_2)$$

Remember that when the SSA applies,

$$k_1A_1X_1 - k_{-1}X_2B_2 \approx k_2A_2X_2 - k_{-2}X_1B_1$$

Rearranging this:

$$X_1 = \left( \frac{k_2A_2 + k_{-1}B_2}{k_1A_1 + k_{-2}B_1} \right) X_2$$

Using the "site balance" above:

$$X_1 = \left( \frac{k_2A_2 + k_{-1}B_2}{D} \right) X_{\text{total}}$$

$$X_2 = \left( \frac{k_1A_1 + k_{-2}B_1}{D} \right) X_{\text{total}}$$

where  $X_{\text{total}}$  is a known constant and

$$D = k_1A_1 + k_2A_2 + k_{-1}B_2 + k_{-2}B_1$$

By applying the SSA to the surface species, we have obtained expressions for the concentrations of the surface species in terms of the concentrations of the fluid-phase species. This lets us eliminate the surface concentrations from the equations. This is helpful because it is much more difficult to measure surface concentrations than it is to measure fluid concentrations. Substituting these expressions into the balance for  $A_1$ , we get:

$$\left( \frac{V}{W_{\text{cat}}} \right) \frac{dA_1}{dt} = r_{A_1} = -X_{\text{tot}}k_1k_2 \left( \frac{A_1A_2}{D} \right) + X_{\text{tot}}k_{-1}k_{-2} \left( \frac{B_1B_2}{D} \right)$$

This result agrees with Boudart's general solution for a multiple-step mechanism of this form ( $A_i + X_i = X_j + B_j$ ) with this approximation applied, where he presents the general solution for  $n \geq 2$  steps: see Eqn. 3.3.9 on p. 69 of Boudart (in the 1991 Butterworth-Heinemann reprint of the original 1968 Prentice-Hall book). An alternate form, for comparison to other cases below, is:

$$\left(\frac{V}{W_{cat}}\right) \frac{dA_1}{dt} = r_{A_1} = -X_{total} K_1 k_2 \left(\frac{A_1 A_2}{K_1 A_1 + B_2 + E}\right) + X_{total} k_{-2} \left(\frac{B_1 B_2}{K_1 A_1 + B_2 + E}\right)$$

where 
$$E = \left(\frac{k_2}{k_{-1}} A_2 + \frac{k_{-2}}{k_{-1}} B_1\right)$$

If we also substitute the relations for  $X_1$  and  $X_2$  into the balance on  $A_2$ , we find that

$$\frac{dA_1}{dt} = \frac{dA_2}{dt}$$

That is, the reactants  $A_1$  and  $A_2$  are consumed at the same rate when the SSA holds for this mechanism.

Before we can integrate the one ODE we now have, we need to express all concentrations in terms of  $A_1$ :

$$\begin{aligned} (A_1^0 - A_1) \propto \text{moles A consumed} &= \text{moles } A_2 \text{ consumed} \\ &= \text{moles } B_1 \text{ produced} \\ &= \text{moles } B_2 \text{ produced} \end{aligned}$$

therefore:

$$A_2 = A_2^0 - (A_1^0 - A_1)$$

$$B_1 = B_1^0 + (A_1^0 - A_1)$$

$$B_2 = B_2^0 + (A_1^0 - A_1)$$

and

$$-r_{A_1} = r_{overall}$$

Finally, after application of the SSA to the surface species, for the reaction pathway

$$A_1 + A_2 = B_1 + B_2 \quad \leftarrow \text{overall stoichiometric equation of reaction pathway}$$

we have an overall, "algebraic" rate expression:

$$\left(\frac{V}{W_{cat}}\right) \frac{dA_1}{dt} = r_{A_1} = -X_{total} k_1 k_2 \left(\frac{A_1 A_2}{D}\right) + X_{total} k_{-1} k_{-2} \left(\frac{B_1 B_2}{D}\right)$$

"forward reaction"      "reverse reaction"

Alternatively, we can write a stoichiometric table in terms of one extent,  $\varepsilon$ , since we only have one stoichiometric degree of freedom left after the SSA, and rewrite our ODE in terms of the initial concentrations and this  $\varepsilon$ .

Before applying the SSA, we needed to integrate two ODEs. After making the SSA, we are left with only one ODE. One of our original ODEs, in effect, was converted into an algebraic equation.

We conclude that application of the SSA to a dynamic reaction system reduced the number of differential equations to be integrated. The cost of this simplification is that the results will be restricted to the limited range of conditions over which the simplifying approximation can be justified.

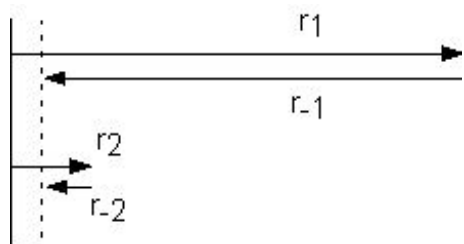
In general for more complex reaction mechanisms, when the SSA is applied to all surface species in the mechanism of an overall reaction pathway, then it may be possible to reduce the system to one ODE with one overall algebraic rate equation. This was possible here. With more complex mechanisms, the algebra required to reduce the system to one overall rate equation will get much more complex.

### Apply the Partial Equilibrium Approximation

In most cases in texts, the SSA is applied at the same time the PEA is applied to all steps except one, the rate determining step (RDS), often without the author stating that the SSA was applied.

Here, in this case, we show that the PEA can be applied in the absence of the SSA. In another case in these notes, we apply both the PEA and the SSA.

We start with no approximations made. We will apply the PEA to elementary step 1 in the reaction mechanism in this example. We justify this when the forward and backward rates of step 1 are each much greater than the net forward rate of step 1:



Boudart says that Kenzi Tamaru introduced him to these sketches. Be careful. This may imply to you that  $K_1 \gg 1$ , i.e., that equilibrium lies far to products on right. It doesn't!  $K_1$  can be  $\ll 1$  and still have this sketch apply. The arrows in the sketch are rates, not the rate coefficients involved in  $K_1$ .

$$r_{1,net} = r_1 - r_{-1}$$

$$\frac{r_{1,net}}{r_1} = \frac{r_1 - r_{-1}}{r_1} = 1 - \frac{r_{-1}}{r_1}$$

$$\frac{r_{-1}}{r_1} = 1 - \frac{r_{1,net}}{r_1} \approx 1 \text{ for } r_{1,net} \ll r_1$$

$$r_1 \approx r_{-1}$$

$$k_1 A_1 X_1 \approx k_{-1} X_2 B_2$$

$$X_1 \approx \frac{k_{-1} X_2 B_2}{k_1 A_1} = \frac{X_2 B_2}{K_1 A_1} \text{ where } K_1 \equiv \frac{k_1}{k_{-1}}$$

From above:

$$B_2 = B_2^0 + (A_1^0 - A_1)$$

$$X_2 = X_1^0 + X_2^0 - X_1 = X_{total} - X_1$$

However, for this case's solution, we must use

$$B_2 = B_2^* + (A_1^* - A_1)$$

We must use the (\*) values of  $A_1$ ,  $B_2$ ,  $X_1$  and  $X_2$  instead of their initial (<sup>0</sup>) values in this solution. The (\*) values are what the concentration values become just after  $t=0$  as the (<sup>0</sup>) values change to establish the required PEA for step 1:

$$A_1^* = A_1^0 - \varepsilon_1^*$$

$$B_2^* = B_2^0 + \varepsilon_1^*$$

$$X_1^* = X_1^0 - \varepsilon_1^* \left( \frac{V}{W_{cat}} \right)$$

$$X_2^* = X_2^0 + \varepsilon_1^* \left( \frac{V}{W_{cat}} \right)$$

where  $\varepsilon_1^*$  is the stoichiometric extent of step 1 required to establish the PEA for step 1:

$$K_1 = \frac{k_1}{k_{-1}} = \frac{B_2^* X_2^*}{A_1^* X_1^*} = \frac{(B_2^0 + \varepsilon_1^*) \left( X_2^0 + \varepsilon_1^* \left( \frac{V}{W_{cat}} \right) \right)}{(A_1^0 - \varepsilon_1^*) \left( X_1^0 - \varepsilon_1^* \left( \frac{V}{W_{cat}} \right) \right)}$$

This is a quadratic equation:

$$a(\varepsilon_1^*)^2 + b\varepsilon_1^* + c = 0$$

$$a = (K_1 - 1) \left( \frac{V}{W_{cat}} \right)$$

$$b = - \left( K_1 X_1^0 + X_2^0 + (K_1 A_1^0 + B_2^0) \left( \frac{V}{W_{cat}} \right) \right)$$

$$c = K_1 A_1^0 X_1^0 - B_2^0 X_2^0$$

The solution is  $\varepsilon_1^*$ :

$$\varepsilon_1^* = \frac{-b - \sqrt{b^2 - 4ac}}{2a} \quad K_1 \neq 1$$

$$\varepsilon_1^* = -\frac{c}{b} \quad K_1 = 1$$

when  $\varepsilon_1^* < A_1^0$ ,  $\varepsilon_1^* > -B_2^0$ ,  $\varepsilon_1^* < X_1^0 \left( \frac{W_{cat}}{V} \right)$ , and  $\varepsilon_1^* > -X_2^0 \left( \frac{W_{cat}}{V} \right)$ . The initial concentrations ( $^0$ ) must allow the PEA to be established for step 1 and for these conditions to be met. Not all initial conditions allow this: e.g.,  $A_1^0 = X_2^0 = 0$ ,  $X_1^0 = B_2^0 = 1$  does not.

Substituting:

$$X_1 \approx \frac{X_2 B_2}{K_1 A_1} = \frac{(X_{total} - X_1)(B_2^* + A_1^* - A_1)}{K_1 A_1}$$

$$X_1 \approx \frac{X_{total}(B_2^* + A_1^* - A_1)}{K_1 A_1} - \frac{X_1(B_2^* + A_1^* - A_1)}{K_1 A_1}$$

$$X_1 \approx \frac{X_{total}(B_2^* + A_1^* - A_1)}{K_1 A_1 + (B_2^* + A_1^* - A_1)}$$

Application of the PEA gives us a relationship between  $X_1$  and  $A_1$ . We can now express all the concentrations in terms of  $A_1$ , including:

$$A_2 = A_2^* - (A_1^* - A_1) + \left( X_1^* - \frac{X_{total}(B_2^* + A_1^* - A_1)}{K_1 A_1 + (B_2^* + A_1^* - A_1)} \right) \left( \frac{W_{cat}}{V} \right)$$

$$B_1 = B_1^* + (A_1^* - A_1) - \left( X_1^* - \frac{X_{total}(B_2^* + A_1^* - A_1)}{K_1 A_1 + (B_2^* + A_1^* - A_1)} \right) \left( \frac{W_{cat}}{V} \right)$$

$$X_2 = \frac{X_{total} K_1 A_1}{K_1 A_1 + (B_2^* + A_1^* - A_1)}$$

The rate of formation of  $A_2$  can be expressed in terms of  $A_1$ :

$$\begin{aligned} r_{A_2} &= -k_2 A_2 X_2 + k_{-2} X_1 B_1 \\ &= -k_2 \left( A_2^* - (A_1^* - A_1) + \left( X_1^* - \frac{X_{total}(B_2^* + A_1^* - A_1)}{K_1 A_1 + (B_2^* + A_1^* - A_1)} \right) \left( \frac{W_{cat}}{V} \right) \right) \left( \frac{X_{total} K_1 A_1}{K_1 A_1 + (B_2^* + A_1^* - A_1)} \right) \\ &\quad + k_{-2} \left( \frac{X_{total}(B_2^* + A_1^* - A_1)}{K_1 A_1 + (B_2^* + A_1^* - A_1)} \right) \left( B_1^* + (A_1^* - A_1) - \left( X_1^* - \frac{X_{total}(B_2^* + A_1^* - A_1)}{K_1 A_1 + (B_2^* + A_1^* - A_1)} \right) \left( \frac{W_{cat}}{V} \right) \right) \end{aligned}$$

The derivative of  $A_2$  can also be expressed in terms of  $A_1$ :

$$\begin{aligned} \frac{dA_2}{dt} &= \frac{d}{dt} \left( A_2^* - (A_1^* - A_1) + (X_1^* - X_1) \left( \frac{W_{cat}}{V} \right) \right) \\ &= \frac{d}{dt} \left( A_2^* - (A_1^* - A_1) + \left( X_1^* - \frac{X_{total}(B_2^* + A_1^* - A_1)}{K_1 A_1 + (B_2^* + A_1^* - A_1)} \right) \left( \frac{W_{cat}}{V} \right) \right) \\ &= \frac{d}{dt} \left( A_2^* - A_1^* + A_1 + \left( X_1^* - \frac{X_{total}(B_2^* + A_1^* - A_1)}{B_2^* + A_1^* + (K_1 - 1)A_1} \right) \left( \frac{W_{cat}}{V} \right) \right) \end{aligned}$$



$$\begin{aligned}
&= \frac{d}{dt} \left( A_1 - \left( \frac{B_2^* + A_1^* - A_1}{B_2^* + A_1^* + (K_1 - 1)A_1} \right) \left( \frac{W_{cat} X_{total}}{V} \right) \right) \\
&= \frac{dA_1}{dt} \left( 1 + \left( \frac{W_{cat}}{V} \right) \left( \frac{X_{total} K_1 (B_2^* + A_1^*)}{(B_2^* + A_1^* + (K_1 - 1)A_1)^2} \right) \right)
\end{aligned}$$

A balance on  $A_2$  gives us:

$$\left( \frac{V}{W_{cat}} \right) \frac{dA_2}{dt} = r_{A_2}$$

Substituting the expressions above,

$$\left( \frac{V}{W_{cat}} \right) \frac{dA_1}{dt} = \frac{-X_{total} K_1 k_2 \left( \frac{A_2 A_1}{K_1 A_1 + B_2} \right) + X_{total} k_{-2} \left( \frac{B_1 B_2}{K_1 A_1 + B_2} \right)}{1 + \left( \frac{W_{cat}}{V} \right) \left( \frac{X_{total} K_1 (B_2^* + A_1^*)}{(B_2^* + A_1^* + (K_1 - 1)A_1)^2} \right)}$$

and continuing to substitute, finally gives us a single ODE to integrate:

$$\left( \frac{V}{W_{cat}} \right) \frac{dA_1}{dt} = \frac{\left( -k_2 \left( A_2^* - (A_1^* - A_1) \right) + \left( X_1^* - \frac{X_{total} (B_2^* + A_1^* - A_1)}{K_1 A_1 + (B_2^* + A_1^* - A_1)} \right) \left( \frac{W_{cat}}{V} \right) \right) \left( \frac{X_{total} K_1 A_1}{K_1 A_1 + (B_2^* + A_1^* - A_1)} \right) + k_{-2} \left( \frac{X_{total} (B_2^* + A_1^* - A_1)}{K_1 A_1 + (B_2^* + A_1^* - A_1)} \right) \left( B_1^* + (A_1^* - A_1) - \left( X_1^* - \frac{X_{total} (B_2^* + A_1^* - A_1)}{K_1 A_1 + (B_2^* + A_1^* - A_1)} \right) \left( \frac{W_{cat}}{V} \right) \right)}{\left( 1 + \left( \frac{W_{cat}}{V} \right) \left( \frac{X_{total} K_1 (B_2^* + A_1^*)}{(B_2^* + A_1^* + (K_1 - 1)A_1)^2} \right) \right)}$$

i.e.,

$$\left( \frac{V}{W_{cat}} \right) \frac{dA_1}{dt} = r_{A_1}$$

The value of  $A_1$  determined at any time can be used to determine the values of all other concentrations at that time.

Application of the PEA to one of the elementary steps in this two-step mechanism (step 1 in this example) replaced one of the ODEs by an algebraic expression.

The right-hand-side of the ODE which remains in this example is an algebraic rate expression for the net rate of generation of  $A_1$ . Note, however, that this is not an overall rate expression for the overall reaction pathway, since  $r_{A_1} \neq r_{A_2}$ :

$$r_{A_1} = \frac{r_{A_2}}{1 + \left(\frac{W_{cat}}{V}\right) \left( \frac{X_{total} K_1 (B_2^* + A_1^*)}{(B_2^* + A_1^* + (K_1 - 1)A_1)^2} \right)}$$

From the relationship between  $A_2$ ,  $A_1$ , and  $X_1$  from the first case with no approximations, for any  $\Delta t$ ,  $\Delta A_2 = \Delta A_1 - \Delta X_1 (W_{cat}/V)$ , where the  $\Delta$ 's are the changes in each concentration in  $\Delta t$ . Both  $\Delta A_2$  and  $\Delta A_1$  are negative. The equation above for the present case shows that  $-r_{A_2} > -r_{A_1}$ , i.e.,  $-\Delta A_2 > -\Delta A_1$ . For this to be true,  $\Delta X_1$  must be positive. This means that, as reaction progresses and the PEA applies,  $X_1$  must increase and  $X_2$  must decrease with increasing time. Let's double-check this by checking the equilibrium PEA relationship on step 1:

$$K_1 = \frac{B_2 X_2}{A_1 X_1} = \frac{B_2 X_2}{A_1 (X_{tot} - X_2)} = \frac{B_2 / A_1}{(X_{tot} - X_2) / X_2}$$

As time increases,  $B_2$  increases and  $A_1$  decreases, so the numerator of the far right expression increases. Therefore, the denominator of the far right expression must increase with time and  $X_2$  must decrease with time.  $X_2$  always decreasing as time increases is consistent with  $-\Delta A_2 > -\Delta A_1$  and  $-r_{A_2} > -r_{A_1}$ .

Note that  $-r_{A_1} \approx -r_{A_2} \approx r_{overall}$  when

$$\left(\frac{W_{cat}}{V}\right) \left( \frac{X_{total} K_1 (B_2^* + A_1^*)}{(B_2^* + A_1^* + (K_1 - 1)A_1)^2} \right) \ll 1$$

$$W_{cat} X_{total} \ll V \left( \frac{(B_2^* + A_1^* + (K_1 - 1)A_1)^2}{K_1 (B_2^* + A_1^*)} \right)$$

Note the similarity between this criterion and the criterion for application of the SSA to the surface species  $X_1$  and  $X_2$ , which was:

$$W_{cat}X_{tot} \ll V(A_1^0 + A_2^0 + B_1^0 + B_2^0)$$

i.e., that the total number of moles of surface species is much less than the total number of moles of fluid-phase species.

Boudart does not consider this case.

Apply both the Steady State Approximation and the Partial Equilibrium Approximation

Let's assume that the following situation applies, i.e., that the PEA applies to step 1 and that both net-forward rates are equal:

$$r_1 \approx r_{-1}$$

$$r_2 > r_{-2}$$

The balance on  $X_1$  is:

$$\frac{dX_1}{dt} = -r_{1,net} + r_{2,net}$$

Since we are assuming that

$$r_{1,net} \approx r_{2,net}$$

we have

$$\frac{dX_1}{dt} \approx 0$$

In addition, the rate of consumption of  $A_1$  equals that of  $A_2$  and it also equals each of the rates of generation of  $B_1$  and  $B_2$ . These are the same results we obtained after we applied the SSA to the surface species.

Therefore, we are now applying the SSA to the surface species and the PEA to step 1.

Step 2 can be called the "rate determining step". Since there are only two elementary steps in this mechanism, applying the PEA to step 1 means we have applied the PEA to all steps except one. The last step becomes the rate determining step. The PEA can't be applied to all steps in a mechanism, since that would fix the system at equilibrium.

When the SSA has been applied to all surface species, and the PEA has been applied to all steps except one, then the right hand side of the one remaining ODE is the rate equation of the overall reaction pathway:

$$\frac{dA_1}{dt} = \frac{dA_2}{dt} = -r_{2,net} = -k_2A_2X_2\left(\frac{W_{cat}}{V}\right) + k_{-2}X_1\left(\frac{W_{cat}}{V}\right)B_1 = -r_{overall}$$

$$\left(\frac{V}{W_{cat}}\right) \frac{dA_1}{dt} = \left(\frac{V}{W_{cat}}\right) \frac{dA_2}{dt} = -r_{2,net} = -k_2 A_2 X_2 + k_{-2} X_1 B_1 = -r_{overall}$$

Now we can substitute the expressions for  $X_1$  and  $X_2$  obtained in the case above where the PEA was applied.

$$r_{overall} = -r_{A_1} =$$

$$X_{total} K_1 k_2 \left( \frac{A_1 A_2}{K_1 A_1 + B_2} \right) \quad \text{"forward rate of overall reaction pathway"}$$

$$- X_{total} k_{-2} \left( \frac{B_1 B_2}{K_1 A_1 + B_2} \right) \quad \text{"reverse rate of overall reaction pathway"}$$

This result agrees with Boudart's solution for a multiple-step mechanism of this form ( $A_i + X_i = X_j + B_j$ ) with these approximations applied, where he presents the general solution for  $n \geq 2$  steps: see Eqn. 4.1.5, p. 84 of Boudart.

All concentrations can be expressed in terms of the concentration of one of the species in order to integrate the one ODE required for this batch reactor under these simplifying assumptions, e.g.,  $A_1$  to integrate the balance on  $A_1$ :

$$\begin{aligned} \left(\frac{V}{W_{cat}}\right) \frac{dA_1}{dt} = & -k_2 \left( A_2^0 - (A_1^0 - A_1) \right) + \left( X_1^0 - \frac{X_{total} (B_2^0 + A_1^0 - A_1)}{K_1 A_1 + (B_2^0 + A_1^0 - A_1)} \right) \left( \frac{W_{cat}}{V} \right) \left( \frac{X_{total} K_1 A_1}{K_1 A_1 + (B_2^0 + A_1^0 - A_1)} \right) \\ & + k_{-2} \left( \frac{X_{total} (B_2^0 + A_1^0 - A_1)}{K_1 A_1 + (B_2^0 + A_1^0 - A_1)} \right) \left( B_1^0 + (A_1^0 - A_1) - \left( X_1^0 - \frac{X_{total} (B_2^0 + A_1^0 - A_1)}{K_1 A_1 + (B_2^0 + A_1^0 - A_1)} \right) \left( \frac{W_{cat}}{V} \right) \right) \end{aligned}$$

To be precise, the (\*) concentrations attained just after  $t=0$  and establishment of PEA in step 1 should be used instead of the (0) initial concentration values (see case with application of PEA but not SSA). However, since the SSA is only justified when the surface capacity is much smaller than the fluid-phase capacity, the difference between the (0) and the (\*) values will be small.

## SUMMARY FOR GENERAL 2-STEP MECHANISM IN A BATCH REACTOR

For all cases below, a stoichiometric table is used to relate the concentrations of the dependent variable(s) to the concentrations of the other species appearing on the right-hand-sides of the equations.

1) No simplifying assumptions - need to integrate two ODEs

$$\frac{dA_1}{dt} = -k_1 A_1 X_1 \left( \frac{W_{cat}}{V} \right) + k_{-1} X_2 \left( \frac{W_{cat}}{V} \right) B_2$$

$$\frac{dX_1}{dt} = -k_1 A_1 X_1 + k_{-1} X_2 B_2 + k_2 A_2 X_2 - k_{-2} X_1 B_1$$

2) Apply SSA to surface species - need to integrate one ODE

$$\left( \frac{V}{W_{cat}} \right) \frac{dA_1}{dt} = r_{A_1} = -X_{total} K_1 k_2 \left( \frac{A_1 A_2}{K_1 A_1 + B_2 + E} \right) + X_{total} k_{-2} \left( \frac{B_1 B_2}{K_1 A_1 + B_2 + E} \right)$$

$$E = \left( \frac{k_2}{k_{-1}} A_2 + \frac{k_{-2}}{k_{-1}} B_1 \right)$$

where

3) Apply PEA to step 1 - need to integrate one ODE

$$\left( \frac{V}{W_{cat}} \right) \frac{dA_1}{dt} = \frac{-X_{total} K_1 k_2 \left( \frac{A_2 A_1}{K_1 A_1 + B_2} \right) + X_{total} k_{-2} \left( \frac{B_1 B_2}{K_1 A_1 + B_2} \right)}{1 + \left( \frac{W_{cat}}{V} \right) \left( \frac{X_{total} K_1 (B_2^* + A_1^*)}{(B_2^* + A_1^* + (K_1 - 1) A_1)^2} \right)}$$

4) Apply PEA to step 1 and apply SSA to surface species - need to integrate one ODE

$$\left( \frac{V}{W_{cat}} \right) \frac{dA_1}{dt} = -X_{total} K_1 k_2 \left( \frac{A_1 A_2}{K_1 A_1 + B_2} \right) + X_{total} k_{-2} \left( \frac{B_1 B_2}{K_1 A_1 + B_2} \right)$$

Of course, since case (4) has the most simplifying assumptions applied, we get the simplest equation to solve.

For cases (2) and (4) above, a single ODE is obtained where the right-hand-side can be considered as the algebraic rate expression for the single overall reaction pathway,  $A_1 + A_2 = B_1 + B_2$ . For case (3) above, the right-hand-side is an algebraic rate expression for the net rate of generation of  $A_1$  but is not an overall rate expression for the overall reaction pathway, since  $r_{A_1} \neq r_{A_2}$ .

Note for cases (3) and (4) above, where the PEA was applied to step 1, only the ratio,  $K_1$ , of the rate coefficients of step 1 appears, not the separate coefficients  $k_1$  and  $k_{-1}$ .

#### References to a few of many articles in which the assumptions of Langmuir-Hinshelwood kinetics do not apply

"Turbulent and stripes wave patterns caused by limited COads diffusion during CO oxidation over Pd(1 1 0) surface: kinetic Monte Carlo studies." A.V. Matveev, E.I. Latkin, V.I. Elokhin and V.V. Gorodetskii, Chemical Engineering Journal, Volume 107, Issues 1-3 , 15 March 2005, Pages 181-189. The dynamic behaviour of the CO oxidation reaction over Pd(1 1 0) has been studied by means of kinetic Monte Carlo modelling. The influence of the internal parameters on the shapes of surface concentration waves obtained in simulations under the limited surface diffusion intensity conditions has been studied. The hysteresis in oscillatory behaviour has been found under step-by-step variation of oxygen partial pressure. Two different oscillatory regimes could exist at one and the same parameters of the reaction. The parameters of oscillations (amplitude, period and the shape of spatio-temporal patterns on the surface) depend on the kinetic prehistory of the system. The possibility for the appearance of the cellular and turbulent patterns, spiral, ring and stripe oxygen waves on the surface in the cases under study has been shown.

"Surface topographical changes and chemical wave patterns in catalytic CO oxidation on Pt(1 1 0)." Han Wei, G. Lilienkamp and R. Imbihl, Chemical Physics Letters, Volume 389, Issues 4-6 , 11 May 2004, Pages 284-288. Chemical wave patterns in catalytic CO oxidation on a Pt(1 1 0) surface have been studied in the 10-5 mbar range using low energy electron microscopy (LEEM) as spatially resolving method. During rate oscillations a cellular pattern develops whose characteristic dimensions are apparently determined by the surface topography of the Pt(1 1 0) surface. Exposure to oscillatory conditions causes a roughening of the surface associated with macroscopic changes in the surface topography.

"Spatiotemporal patterns during CO oxidation on Pt(100) at elevated pressures." Lele, TP; Pletcher, TD; Lauterbach, J., AIChE JOURNAL, JUN, 2001, V47(N6):1418-1424. CO oxidation on Pt(100) was investigated at reactant pressures of 8 Pa using ellipsomicroscopy for surface imaging to monitor spatiotemporal pattern formation on the catalyst surface and mass spectroscopy to monitor the integral reaction rate. Three distinct temperature regions showing nonlinear phenomena were found. The first region, at 540-615 K, is characterized by macroscopic, regular reaction-rate oscillations with spatially uniform, instantaneous transitions between CO and oxygen covered states. Regular, periodic oscillations were not observed on Pt(100) before. The second region, 480-540 K, exhibited continuous dynamic pattern formation with no visible macroscopic kinetic oscillations. Front speeds measured indicated a decrease in oxygen front velocity and an increase in CO front velocity with an increasing CO/O<sub>2</sub> partial pressure ratio. The third region, 390-430 K, is characterized by macroscopic rate oscillations, which continued for several oscillation periods and then ceased with the onset of pattern formation.

"Imaging Pattern Formation in Surface Reactions from Ultrahigh Vacuum up to Atmospheric Pressures." Rotermund, H.H.; Haas, G.; Franz, R.U.; Tromp, R.M.; Ertl, G.; Science, vol. 270, pp. 608 (1995).

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TITLE: The interaction of CO and Pt(100). I. Mechanism of adsorption and Pt phase transition  
SOURCE: Behm, R.J.; Theil, P.A.; Norton, P.R.; Ertl, G.; J. Chem. Phys., vol. 78, pp. 7437 (1983).  
NOTES: Reconstruction of the surface caused by adsorption  
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TITLE: Oscillatory kinetics in heterogeneous catalysis  
SOURCE: Imbihl, R.; Ertl, G.; Chem. Rev., vol. 95(3), pp. 697-734 (1995).  
NOTES: In Chemical Reviews special issue on "Heterogeneous Catalysis."  
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TITLE: Imaging pattern formation in surface reactions from ultrahigh vacuum up to atmospheric pressures  
SOURCE: Rotermund, H.H.; Haas, G.; Franz, R.U.; Tromp, R.M.; Ertl, G.; Science, vol. 270, pp. 608-610 (1995).  
NOTES: Two optical techniques for imaging adsorbed species on crystal surfaces under significant gas pressure: reflection anisotropy microscopy (RAM) and ellipsomicroscopy (EMSI). Shows pattern formation during CO oxidation over Pt(110) from 1E-4 to 1 mbar.  
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TITLE: Effects of boundaries on pattern formation: Catalytic oxidation of CO on platinum  
SOURCE: Graham, M.D.; Kevrekidis, I.G.; Asakura, K.; Lauterbach, J.; Krischer, K.; Rotermund, H.-H.; Ertl, G.; Science, vol. 264, pp. 80-82 (1994).  
NOTES: Fantastic paper with lots of photoemission electron microscopy (PEEM) photos of traveling waves and patterns on various shapes of Pt surfaces made by covering the Pt surface with a Ti layer and then etching a pattern in the Ti layer to expose Pt. The Pt surface shapes (rings, Tees) have a size of about 80-350 micrometers.  
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TITLE: Spirals and propagating reaction fronts during catalytic CO oxidation on a cylindrical Pt single crystal  
SOURCE: Sander, M.; Vesper, G.; Imbihl, R.; J. Vac. Sci. Technol. A, vol. 10, pp. 2495-2500 (1992).  
NOTES: Beautiful PEEM pictures!!!! ABSTRACT: "The spatiotemporal patterns that are associated with kinetic oscillations in the catalytic CO oxidation have been investigated on a Pt single crystal of cylindrical shape whose axis is oriented in the [001] direction. The experiments were conducted in the 10<sup>-5</sup> and 10<sup>-4</sup> Torr range between 450 and 550 K using a photoemission electron microscope for imaging the spatial adsorbate distribution during the reaction. The cylinder surface exhibits all orientations of the [001] zone including (100), (110), and (210) whose oscillatory behavior has been studied before. On Pt(100) rotating spirals, target patterns, and ordered arrays of reaction fronts are observed, but these regular patterns were confined to a narrow orientational range of  $\pm 2^\circ$  around (110). Further away fluctuating irregular patterns are found which finally merge into the oxygen-covered surface characteristic of the more active orientations around (210). Under appropriate conditions kinetic oscillations can be found on (210) which are again associated with spatial pattern formation. The transition from a CO-covered to an oxygen-covered surface proceeds via a propagating reaction front, while the transition in the reverse direction takes place through the growth of small CO islands distributed randomly across the surface. Finally, an oscillation mode has been found in which the phase boundaries separating the oxygen-covered active zone from the inactive CO-covered zone on the cylinder surface periodically shifts thus causing expansion/contraction cycle of the active zone. The phase boundary in between (210) and (100) can also act as a source for oxygen islands which are detached from the phase boundary and then shrink while traveling as a whole towards (100)."  
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TITLE: Oscillatory catalytic reactions at single crystal surfaces  
SOURCE: Ertl, G.; in Advances in Catalysis, Edition 37, Eley, D.D., Ed., pp. 213-273 (1991).  
NOTES: S&E: QD1/A244/v. 37  
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TITLE: Oscillatory kinetics and spatio-temporal self-organization in reactions at solid surfaces

SOURCE: Ertl, G. ; Science, vol. 254, pp. 1750-1755 (1991).

NOTES: Great article!

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TITLE: Chemical reaction fronts on platinum surfaces

SOURCE: Mundschau, M.; Rausenberger, B.; ; Platinum Metals Rev., vol. 35, pp. 188-195 (1991).

NOTES: ABSTRACT: "In many chemical reactions catalysed on platinum surfaces it is necessary that two reactants be adsorbed simultaneously. Often one reactant is so strongly adsorbed that it blocks the adsorption of the second; such a reaction is said to be self-poisoning. An example is the oxidation of carbon monoxide, where carbon monoxide forms a strongly adsorbed monolayer which effectively blocks the adsorption and decomposition of oxygen. Photoelectron microscopy shows, however, that oxygen can penetrate the carbon monoxide film at special defect sites, typically inclusions or microdust particles, on the platinum. From these special adsorption sites the oxygen rapidly reacts with neighboring adsorbed carbon monoxide. Reaction fronts initiate at these sites and rapidly propagate across the surface. A second type of self-poisoning occurs in decomposition reactions for which vacant surface sites are necessary; for instance, the decomposition of nitric oxide in the presence of hydrogen. A monolayer film of nitric oxide poisons the reaction not by blocking the adsorption of hydrogen, but rather by preventing the dissociation of nitric oxide which requires a neighboring unoccupied surface site. Empty sites are provided on impurity particles which weakly adsorb nitric oxide and initiate reaction fronts. Impurity sites also initiate reaction fronts when graphite is removed from platinum by oxidation. In order to avoid self-poisoning in catalytic reactions, these studies suggest that special adsorption sites should be introduced artificially to provide vacant sites by adsorbing only weakly the reactants causing self-poisoning."

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TITLE: Spatiotemporal concentration patterns in a surface reaction: propagating and standing waves, rotating spirals, and turbulence

SOURCE: Jakubith, S.; Rotermund, H.H.; Engel, W.; Von Oertzen, A.; Ertl, G.; Phys. Rev. Lett., vol. 65, pp. 3013-3016 (1990).

NOTES: Waves and spirals measured by PEEM over area 0.2 X 0.3 mm look to have wavelengths about 20 microns and propagation speeds of 1-3 micron/s. Also can get standing wave patterns that oscillate with periods of about 1-3 s and shapes like ovals or rectangular bars. Beautiful!

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TITLE: A scanning tunneling microscopy investigation of the  $1 \times 2 = 1 \times 1$  structural transformation of the Pt(110) Surface

SOURCE: Gritsch, T.; Coulman, D.; Behm, R.J.; Ertl, G.; Appl. Phys. A, 49, 403-406 (1989).

NOTES: ABSTRACT: Lifting of the reconstruction of the clean Pt(110) surface under the influence of adsorbed CO proceeds at 300K through homogeneous nucleation of small "holes" (with about 10 X 10 square Angstrom size). At 350K more correlated displacements of (110) strings takes place, a characteristic shared with the reverse process, namely the restoration of the  $1 \times 2$  phase after desorption. "The surface structure of the clean (110) surfaces of Ir, Pt, and Au is of the "missing row" type. Calculations for Au(110) revealed, however, that the total energy of this  $1 \times 2$  phase is only about 6% lower than that of the non-reconstructed  $1 \times 1$  phase. Hence mutual structural transformations may become energetically feasible under the influence of an adsorbate and are in fact frequently observed." "The Pt crystal was mounted on a molybdenum sampled holder with platinum foil strips." "The Pt(110) crystal was cleaned by alternate argon ion bombardment (700 eV, 1.5 micro-A) at 300K for about one hour, oxidation in  $5 \times 10^{-4}$  Pa oxygen at 700K and annealing at 1000K."

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TITLE: Imaging of spatio-temporal pattern evolution during carbon monoxide oxidation on platinum

SOURCE: Rotermund, H.H.; Engel, W.; Kordesch, M.; Ertl, G.; Nature, vol. 343, pp. 355-357 (1990).

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TITLE: Real-time observation of the nucleation and propagation of reaction fronts on surfaces using photoemission electron microscopy



SOURCE: Mundschaum, M.; Kordesch, M.E.; Rausenberger, B.; Engel, W.; Bradshaw, A.M.; Surface Science 227, 246-260 (1990).

NOTES: Quote from text (Abstract follows): The general concept of the reaction front in CO oxidation was expressed already in 1921 by Langmuir [ref] who remarked "that the exposure of the 'flanks' of an adsorbed film to attack by colliding molecules would render them much more susceptible to chemical action" and that "the film would be removed progressively from its bounding edge inward." He also observed that there was no experimental evidence for such fronts at that time, although much indirect evidence made it reasonable to assume that many reactions could only take place at the boundary between the two (surface) phases.

ABSTRACT: The catalytic oxidation of CO on Pt(100) has been studied in situ using photoemission electron microscopy (PEEM). The difference in work function between CO-covered regions of the surface and O-covered regions provides image contrast in PEEM using a deuterium lamp. The CO and O<sub>2</sub> partial pressures were adjusted to give a CO coverage greater than 0.5 monolayer at a crystal temperature below 500 K corresponding to the low rate branch of the oxidation reaction in which CO inhibits the adsorption of oxygen. The transition to the high rate branch (characterized by low CO coverage) was then initiated by decreasing the CO partial pressure. This allows oxygen adsorption at various types of defect sites, forming holes in the CO film. The holes subsequently enlarge as reaction fronts propagate away from the defect sites, forming holes in the CO film. The holes subsequently enlarge as reaction fronts propagate away from the defects at velocities from 0.5 to 40 micrometers per second, depending on temperature, pressure and directions of steps on the surface. The return to the low rate branch, induced by increasing the CO pressure again, does not give rise to propagating reaction fronts but rather to random adsorption of CO throughout the surface.

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TITLE: Forced oscillations of a self-oscillating surface reaction

SOURCE: Eiswirth, M.; Ertl, G.; Phys. Rev. Lett. 60, 1526-1529 (1988).

NOTES: Pt(110) used. "Because of this high sensitivity to changes of the partial pressures, periodic forcing of the system could be achieved by low-amplitude (about 1%) modulation of pO<sub>2</sub>." "In conclusion, this work describes the first well-defined example of a heterogeneous surface reaction showing the features developed for self-oscillating chemical reactions under the influence of periodic perturbations."

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TITLE: Kinetic oscillations during the catalytic carbon monoxide oxidation on palladium (110): the role of subsurface oxygen

SOURCE: Ladas, S.; Imbihl, R.; Ertl, G.; Surf.Sci., vol. 219, pp. 88-106 (1989).

NOTES: At high O pressures (pO<sub>2</sub> > 1 .times. 10<sup>-3</sup> Torr) and at fairly low temp. (T = 400 K) the catalytic CO oxidn. on Pd(110) exhibits kinetic oscillations which were followed by means of measurements of the reaction rate and of the work function change. Under these conditions the kinetics of CO<sub>2</sub> formation develop pronounced hysteresis effects which differ significantly from those obsd. with Pt surfaces. The unusual features in the CO<sub>2</sub> hysteresis could be related to the formation of subsurface O which has been demonstrated to take place under the same conditions. As subsurface O decreases the catalytic activity of the surface, the characteristic hysteresis effects could be traced back to a slow filling and depleting of the subsurface O reservoir under conditions of varying adsorbate coverages. A mechanism for the kinetic oscillations on Pd(110) is suggested in which the slow formation/removal of subsurface O modulates the catalytic activity of the surface. The operation of a mechanism which is based on structural changes, e.g. a surface phase transition or reversible faceting, can be excluded on the basis of the property of the clean Pd(110) surface which does not reconstruct, as well as from the absence of kinetic oscillations in the low pressure regime (pO<sub>2</sub> < 1 .times. 10<sup>-3</sup> Torr).

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TITLE: Microfacetting of a platinum(110) surface during catalytic carbon monoxide oxidation

SOURCE: Ladas, S.; Imbihl, R.; Ertl, G.; Surf.Sci., vol. 197, pp. 153-182 (1988).

NOTES: The integral LEED spots from a Pt(110) surface continuously split and broadened during catalytic oxidn. of CO if the conditions were adjusted in a way that the 1 .times. 2 reconstruction of the surface was lifted

by adsorbed CO. This effect is due to the formation of microfacets in the [001] zone (and to a lesser extent in the [110] zone) and is accompanied by a continuous increase of the catalytic activity. This increase is traced to an enhanced O sticking coeff. (under the conditions of high CO coverage) on the faceted surface. The tendency for faceting is counterbalanced by that for thermal reordering which increases with increasing temp. The nucleation of the facets is linked to the creation of sites assocd. with the  $1 \times 2$   $\sqrt{3} \times \sqrt{3}$  surface phase transition, though several possibilities exist for their growth mechanism.

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