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When are Two Eyes Better than One: Model Construction vs Model Reduction

Rutherford Aris (1929 – 2005)

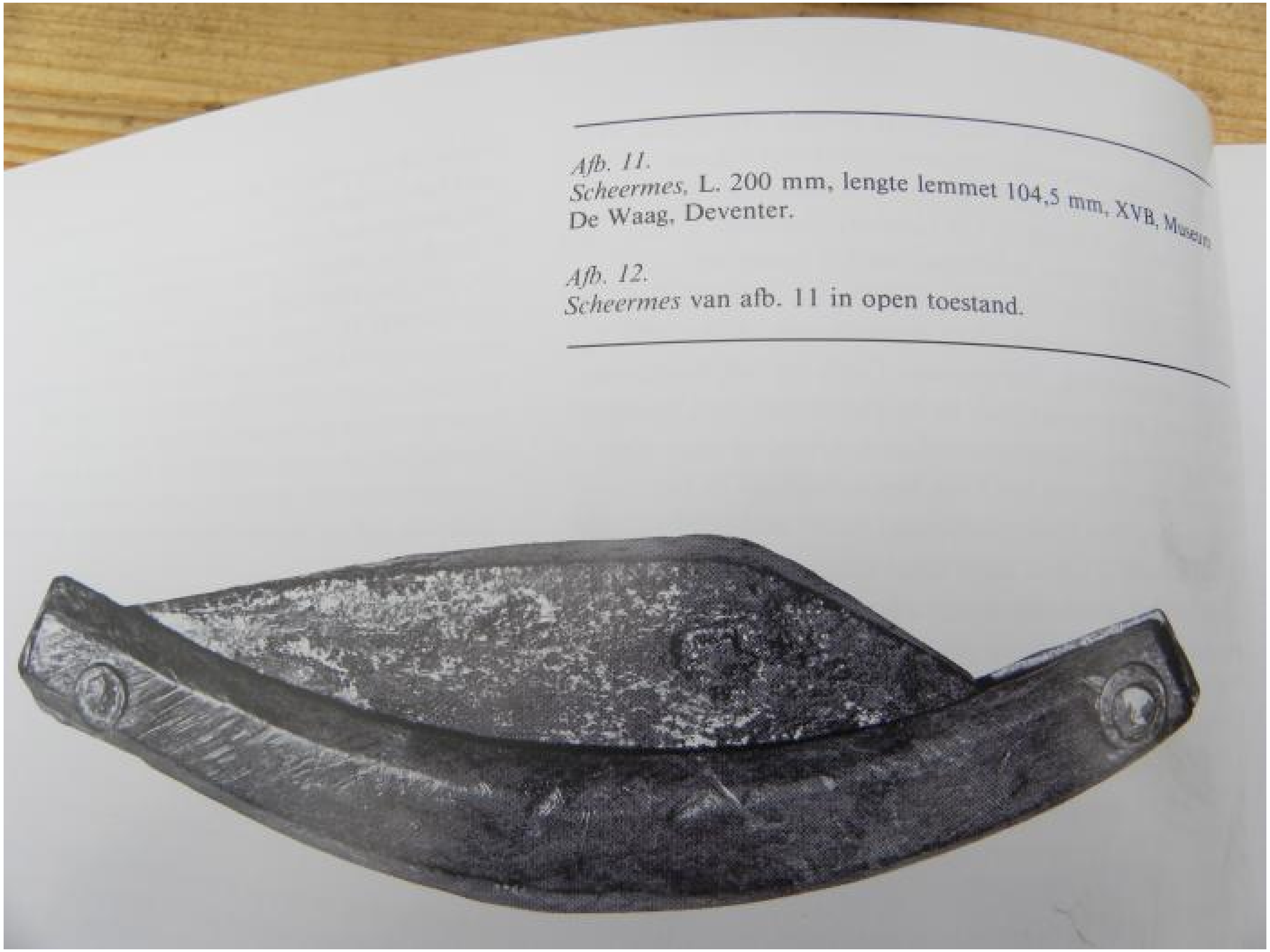
The most remarkable coincidence in my life

- **“TWO EYES ARE BETTER THAN ONE:**
- some reflections on the importance to have more than one viewpoint in mathematical disciplines or other disciplines”,
- *Mathl. Comput.Modelling*, Vol.18, No.8, pp. 95-113, 1993

Pomona, the Roman Goddess of Fruitful Abundance

William of Occam (1288-1348)

Occam's razor



Occam's Razor

Entia non sunt multiplicanda praeter necessitatem

(entities must not be multiplied beyond necessity)

- These words attributed to Ockham are absent in his extant works

Bonsai Tree as a Model

Origami Bonsai Tree as a Ideal Scientific Model

Outline

- Introduction
- Concepts and experimental devices
- Models
- Chemical Calculus:
- TAP-experiments and data analysis
- CO oxidation
- Conclusions

Reaction mechanism or mechanism:

- Fundamental concept of chemical kinetics
- Comprehensive interpretation of all experimental data accumulated on a complex reaction process
- Includes a detailed description of the steps leading from the reactants to the products of a reaction

G.B. Marin & G.S. Yablonsky (2011).

Oxydation of Hydrogen

$$2\,H_2 + O_2 \rightleftharpoons 2\,H_2O$$

- 5 intermediates: $H\cdot$, $O\cdot$, $OH\cdot$, $HO_2\cdot$, H_2O_2
- 30 elementary steps

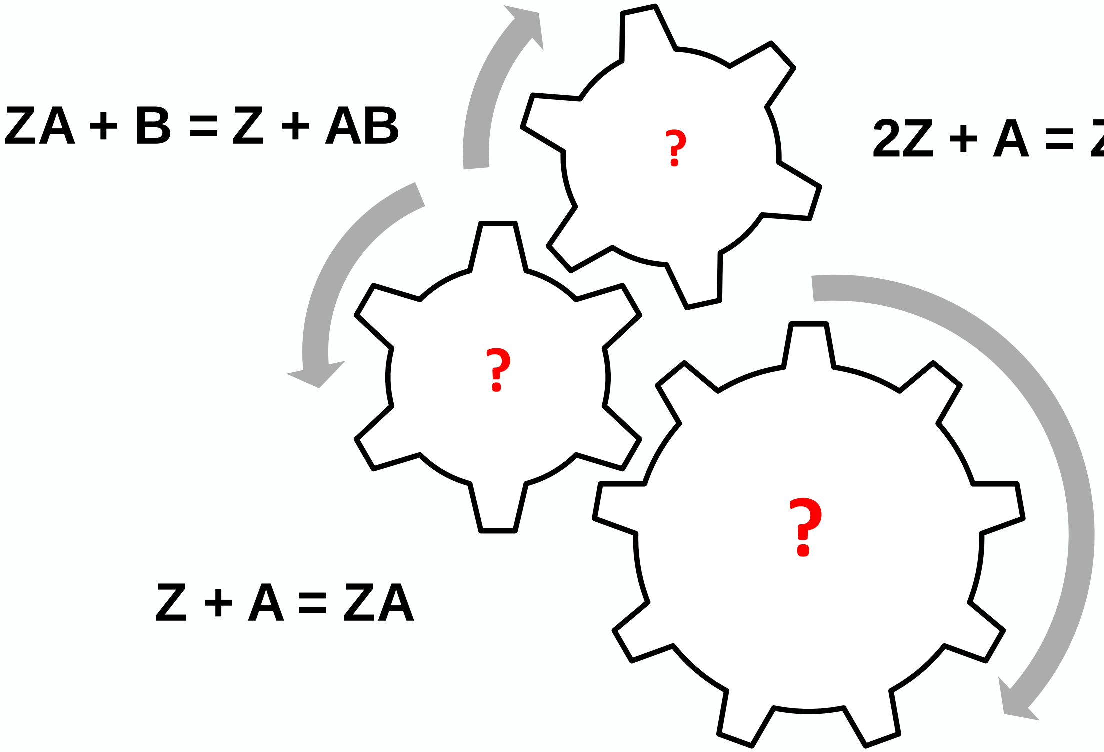
G.B. Marin & G.S. Yablonsky (2011).

Chemical Kinetics
Textbook Knowledge (3)

- Detailed mechanism is a set of elementary reactions which law is assumed , e. g. the mass-action-law
- An example: **Hydrogen Oxidation $2H_2 + O_2 = 2H_2O$**

- 1) $H_2 + O_2 = 2\,OH$; 2) $OH + H_2 = H_2O + H$; 3) $H + O_2 = OH + O$;
- 4) $O + H_2 = OH + H$; 5) $O + H_20 = 2OH$; 6) $2H + M = H_2 + M$; 7) $2O + M = O_2 + M$;
- 8) $H + OH + M = H_2O + M$; 9) $2\,OH + M = H_2O_2 + M$; 10) $OH + O + M = HO_2 + M$;
- 11) $H + O_2 + M = HO_2 + M$; 12) $HO_2 + H_2 = H_2O_2 + H$;13) $HO_2 + H_2 = H_2O + OH$;
- 14) $HO_2 + H_2O = H_2O_2 + OH$; 15) $2HO_2 = H_2O_2 + O_2$; 16) $H + HO_2 = 2\,0H$;
- 17) $H + HO_2 = H_2O + O$; 18) $H + HO_2 = H_2 + O_2$; 19) $O + HO_2 = OH + H$;
- 20) $H + H_2O_2 = H_20 + OH$; 21) $O + H_2O_2 = OH + H0_2$; 22) $H_2 + O_2 = H_20 + O$;
- 23) $H_2 + O_2 + M = H_20_2 + M$; 24) $OH + M = O + H + M$; 25) $HO_2 + OH = H_2O + O_2$;
- 26) $H_2 + O + M = H_2O + M$; 27) $O + H_2O + M = H_20_2 + M$; 28) $O + H_2O_2 = H_20 + O_2$;
- 29) $H_2 + H_2O_2 = 2H_2O$; 30) $H + HO_2 + M = H_2O_2 + M$

Catalyst and process design require **reliable microkinetic models** of catalytic reactions …



Methane Steam Reforming

Overall reactions:

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

$$(1) \quad CH_4 + Z \rightleftharpoons CH_2Z + H_2$$

$$(2) \quad CH_2Z + H_2O \rightleftharpoons CHOHZ + H_2$$

$$(3) \quad CHOHZ \rightleftharpoons COZ + H_2$$

$$(4) \quad COZ \rightleftharpoons Z + CO$$

$$(5) \quad Z + H_2O \rightleftharpoons OZ + H_2$$

$$(6) \quad OZ + CO \rightleftharpoons Z + CO_2$$

active site

surface intermediate

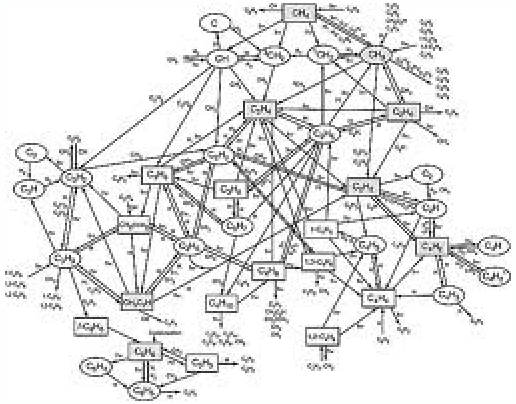
G.B. Marin & G.S. Yablonsky (2011).

Catalyst and process design require **reliable microkinetic models** of catalytic reactions …

Prior knowledge

Theoretical predictions

Combinatorics



Exhaustive reaction network

Which subset is kinetically important in my experiment?

Approaches to model discrimination:

- **Regression of data** using the entire network or multiple rival models.
- Search for **kinetic fingerprints** within the network and construction of **minimal reaction mechanism**.

G. B. Marin & G. S. Yablonksy (Wiley-VCH, 2011)

Approaches to model discrimination:

- **Regression of data** using the entire network or multiple rival models.
- Search for **kinetic fingerprints** within the network and construction of **minimal reaction mechanism**.

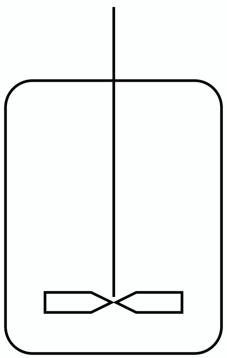
⇓

More tractable microkinetic models

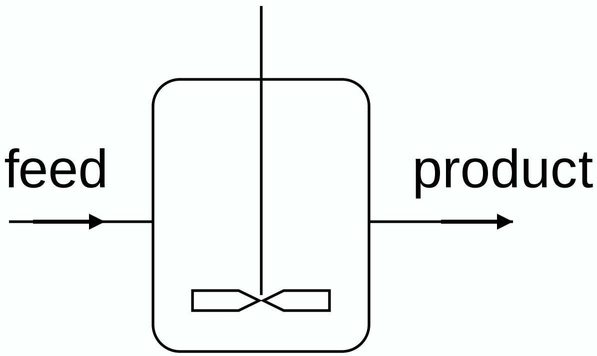
G. B. Marin & G. S. Yablonksy (Wiley-VCH, 2011)

Reactors for Kinetic Experiments

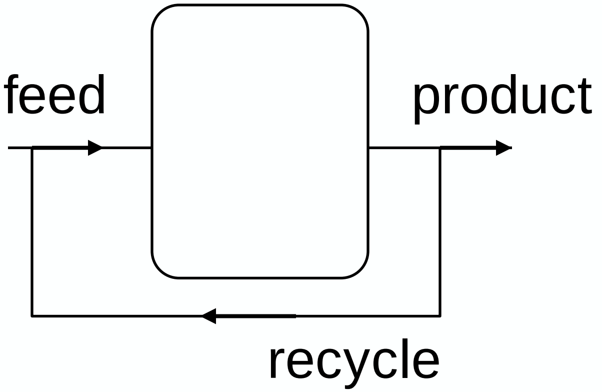
Batch reactor



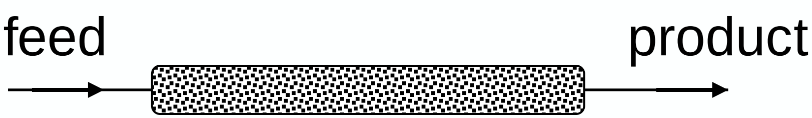
CSTR



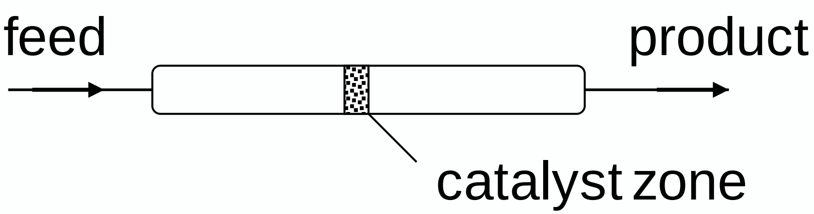
Continuous-flow reactor with recirculation



PFR

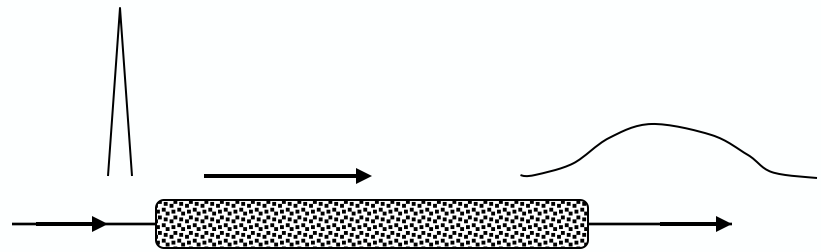


Differential PFR

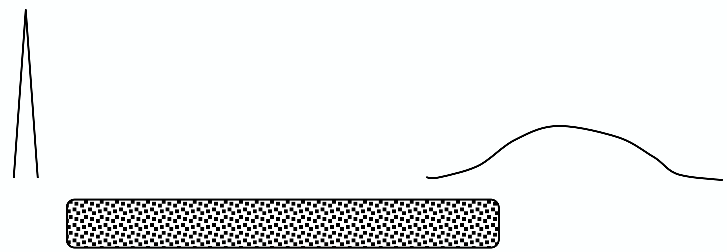


Reactors for Kinetic Experiments

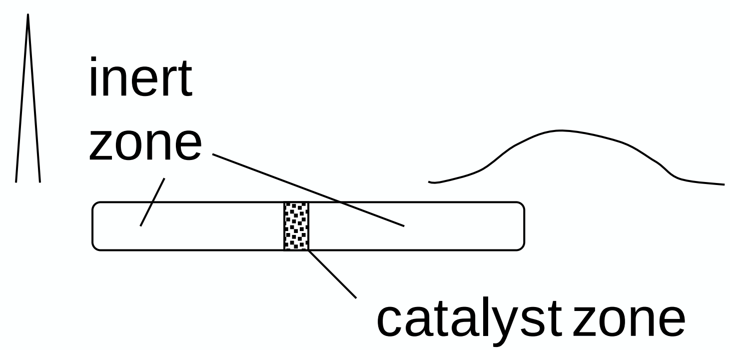
Convectional pulse
reactor



Diffusional pulse
reactor / TAP
reactor



Thin-zone TAP
reactor



Non-Steady-State Models

$$\frac{d\mathbf{c}}{dt} = f\left(\mathbf{c}, \mathbf{k}\right)$$

describes the temporal evolution of a chemical reaction mixture from an initial state to a final state

- closed system: *equilibrium*
- open system: *steady state*

Three methods for studying non-steady-state behavior:

- change in time t: change in dynamic space $(\mathbf{c},t)$
- change of parameters $\mathbf{k}$: change in parametric space $(\mathbf{c},\mathbf{k})$
- change of a concentration with respect to others: change in phase space

Kinetic Model-Free Analysis

Reactor Model:

Accumulation - Transport Term = Reaction Rate

Batch Reactor:	Non	$V_g \frac{dC}{dt} = R \cdot S$
CSTR:	Convection	$V_g \frac{dC}{dt} - V(C^0 - C) = R \cdot S$
PFR:	Convection	$V_g \frac{\partial C}{\partial t} - v \frac{\partial C}{\partial x} = R \cdot S$
TAP:	Diffusion	$V_g \frac{\partial C}{\partial t} - V_r D \frac{\partial^2 C}{\partial x^2} = R \cdot S$

I. STOP TIME !

II. Chemical Calculus

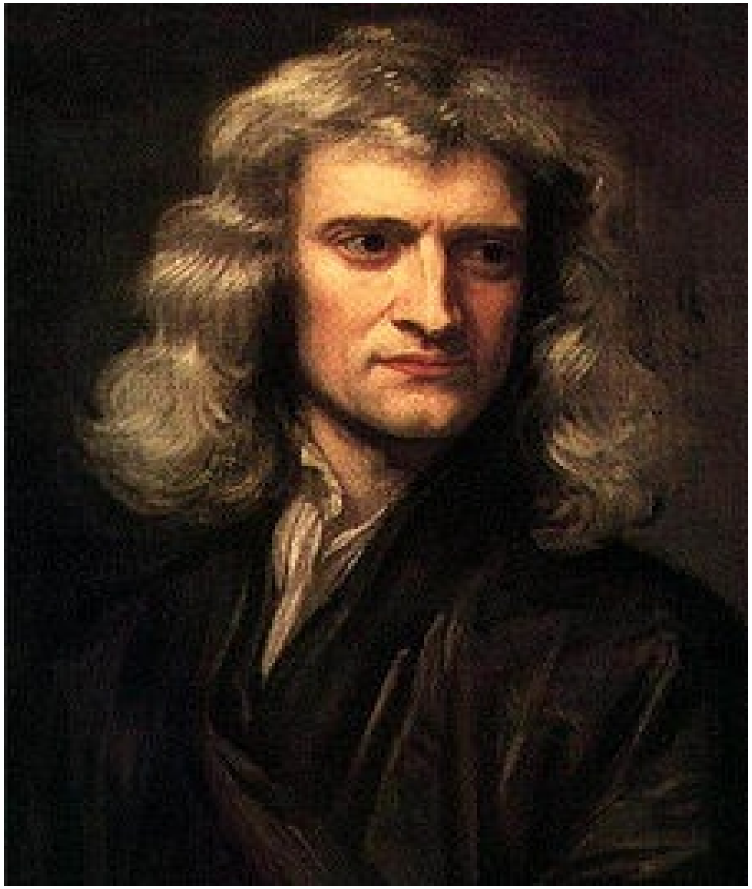
Founders of infinitesimal calculus:

Newton and Leibnitz

Calculus' foundation: Cavalieri is a precursor of infinitesimal calculus

In Europe, the foundational work was a treatise due to Bonaventura Cavalieri, who argued that volumes and areas should be computed as the sums of the volumes and areas of infinitesimal thin cross-sections

Isaac Newton (1642-1727)



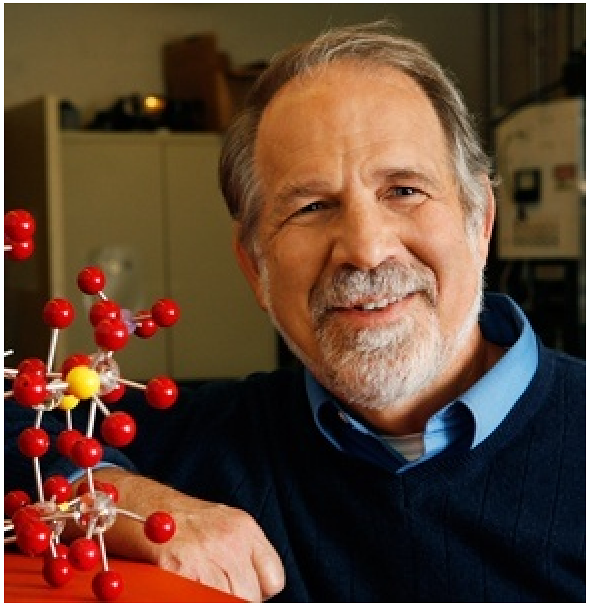
Gottfried Wilhelm Leibnitz (1646-1716)

‘Drop-by-drop’: titration, determination of the equivalent point

The origins of volumetric analysis are in late-18th-century French chemistry. Francois Antoine Henri Descroizilles developed the first burette (which looked more like a graduated cylinder) in 1791. Joseph Louis Gay-Lussac developed an improved version of the burette that included a side arm, and coined the terms "pipette" and "burette" in an 1824 paper on the standardization of indigo solutions

Manfred Eigen (1927): Chemical relaxation, but not calculus

Experimental chemical calculus : John T. Gleaves



- **Temporal Analysis of Products (TAP)**, a vacuum transient response experiment performed by injecting a small number of gas molecules into an evacuated reactor containing a solid sample, which provides precise kinetic characterization of gas-solid interactions with submillisecond time resolution (developed by J.T. Gleaves in 1988)

Non-Steady-State Catalytic Processes

- Automotive catalytic processes
- Reverse-flow processes
- Oxidation-reduction processes for selective hydrocarbon oxidation
- Circulating fluidized-bed reactors
- Chemical looping combustion (CLC)

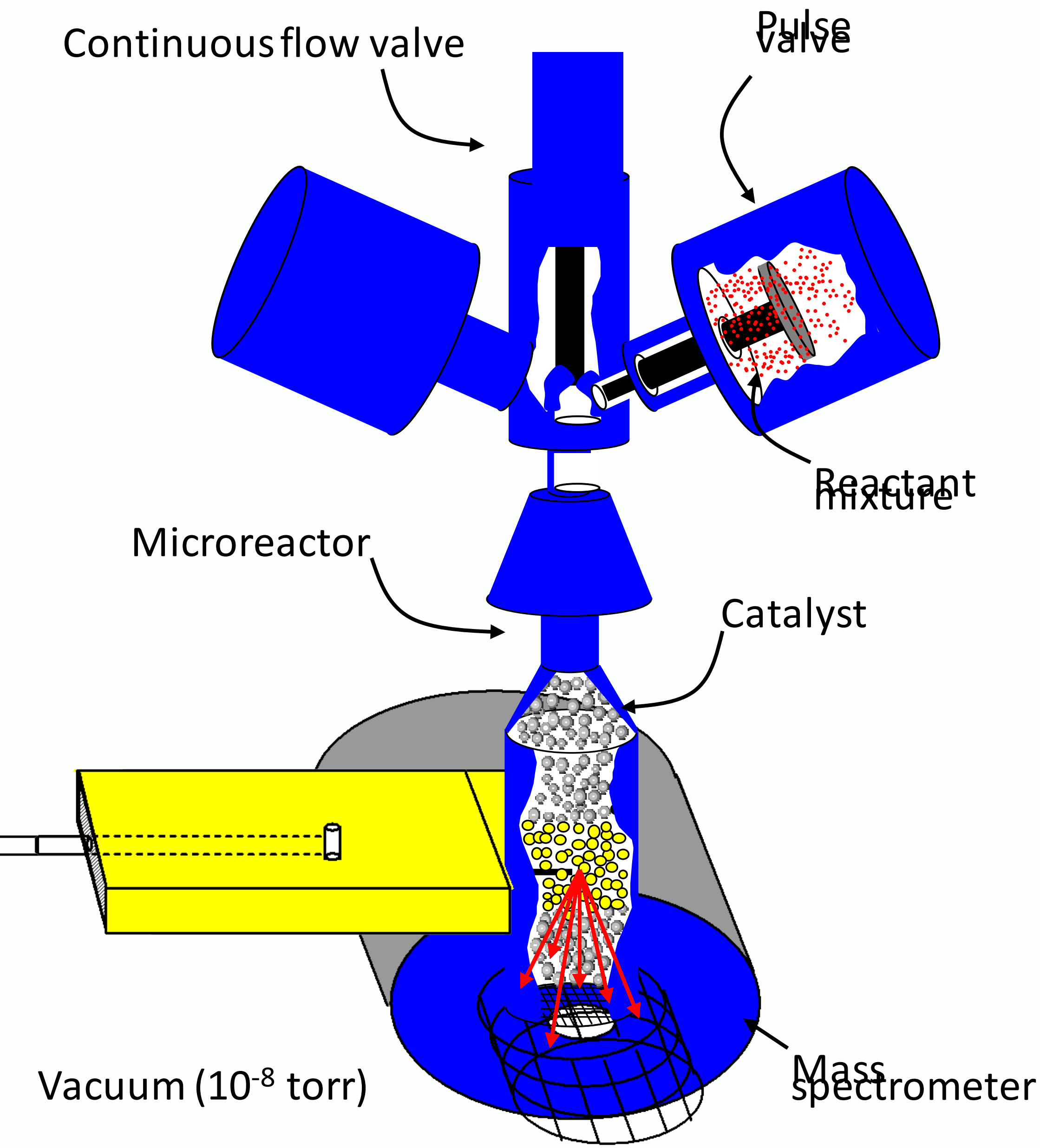
  (total oxidation of hydrocarbons by metal oxides)

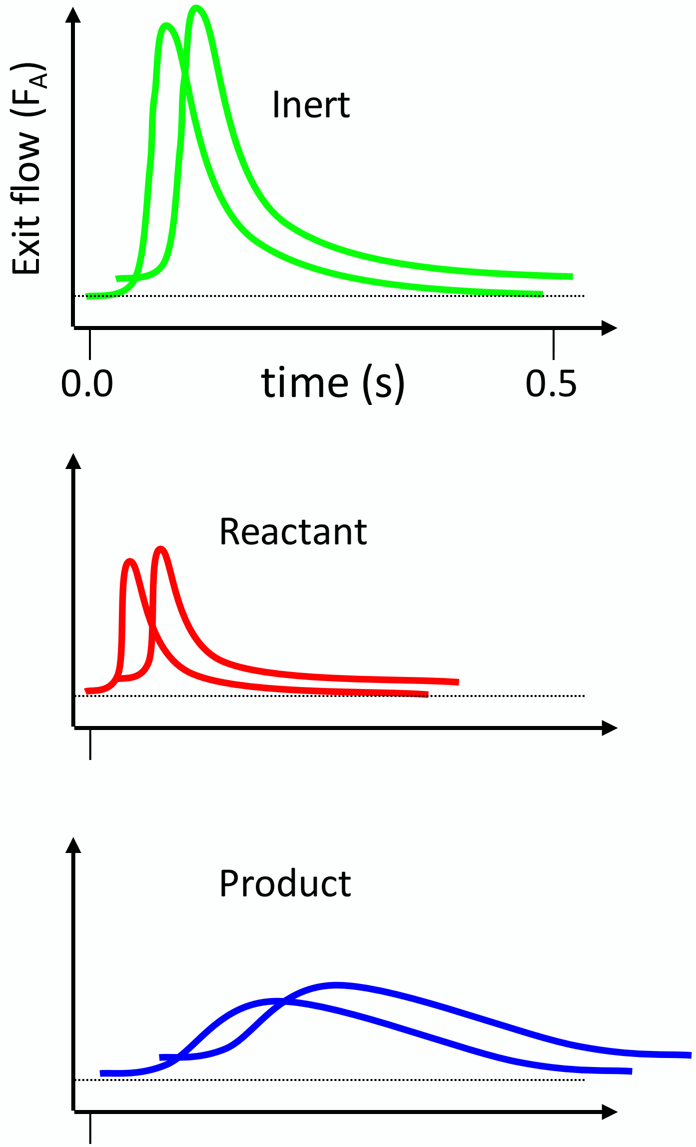
Non-Steady-State Kinetic Screening

TAP: Temporal Analysis of Products

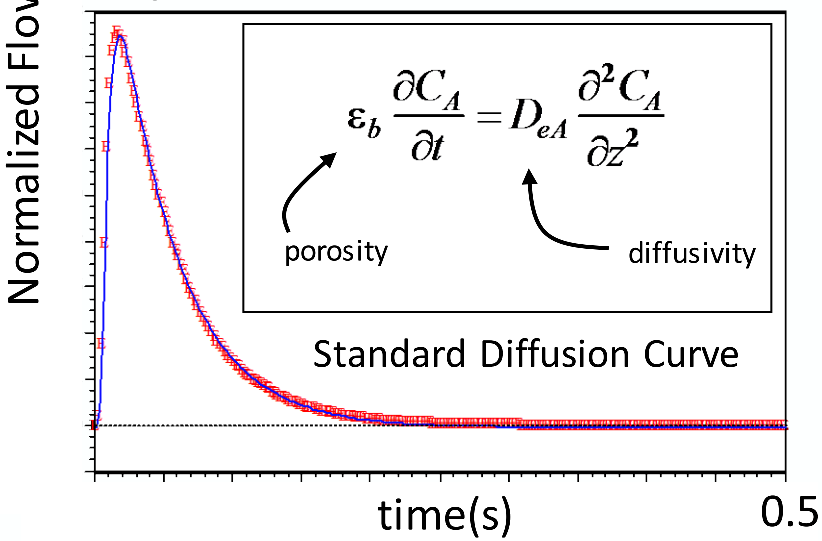
- Series of pulses of very small intensity
- Change of catalyst composition in controlled manner
- Sequence of *infinitesimal* steps produces a *finite* change $\rightarrow$ “chemical calculus”

TAP Reactor System-Overview

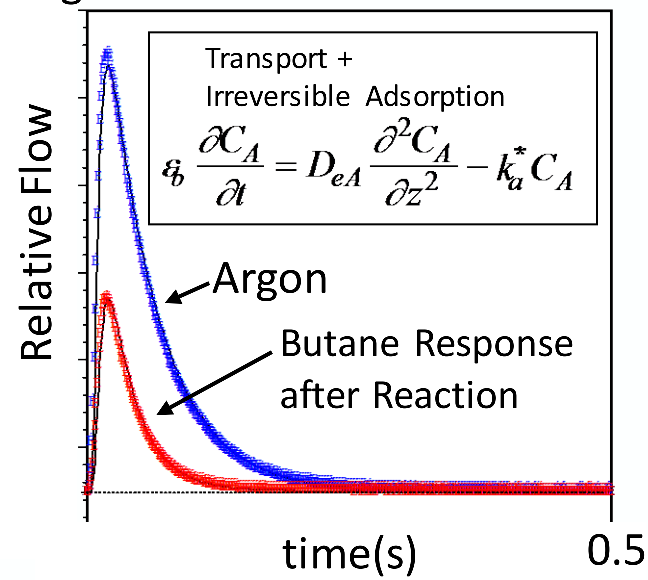




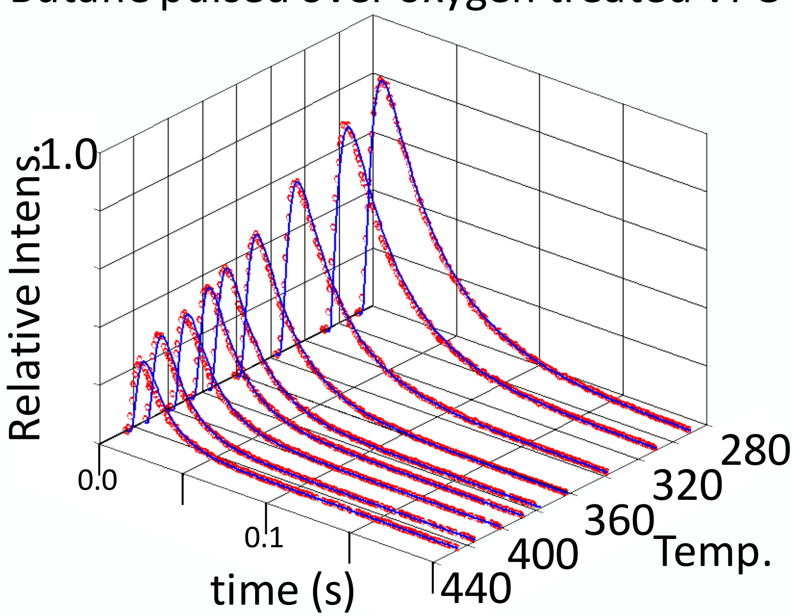
Experimental and Predicted Responses
Argon Pulsed over Quartz Particles



Experimental and Predicted Responses
Argon and Butane Pulsed over VPO



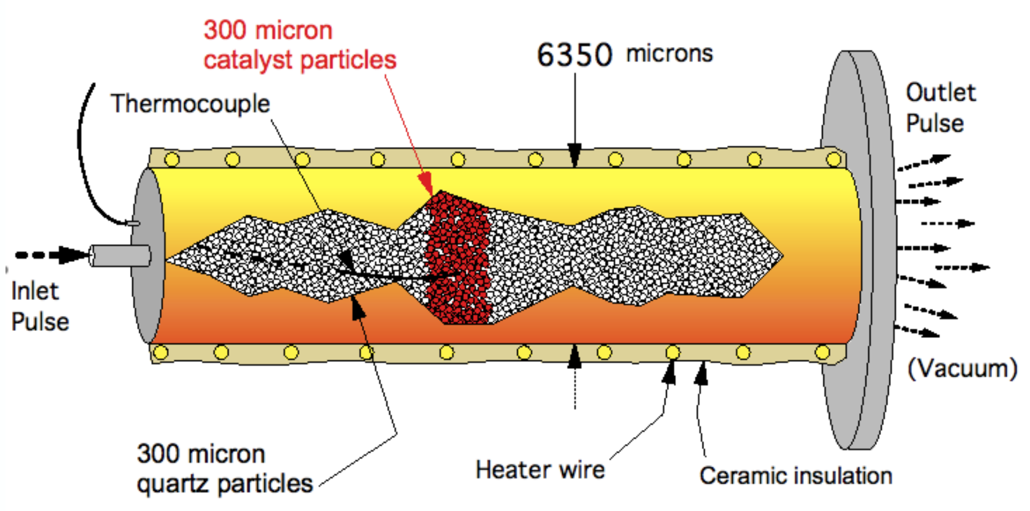
Experimental and predicted responses
Butane pulsed over oxygen treated VPO



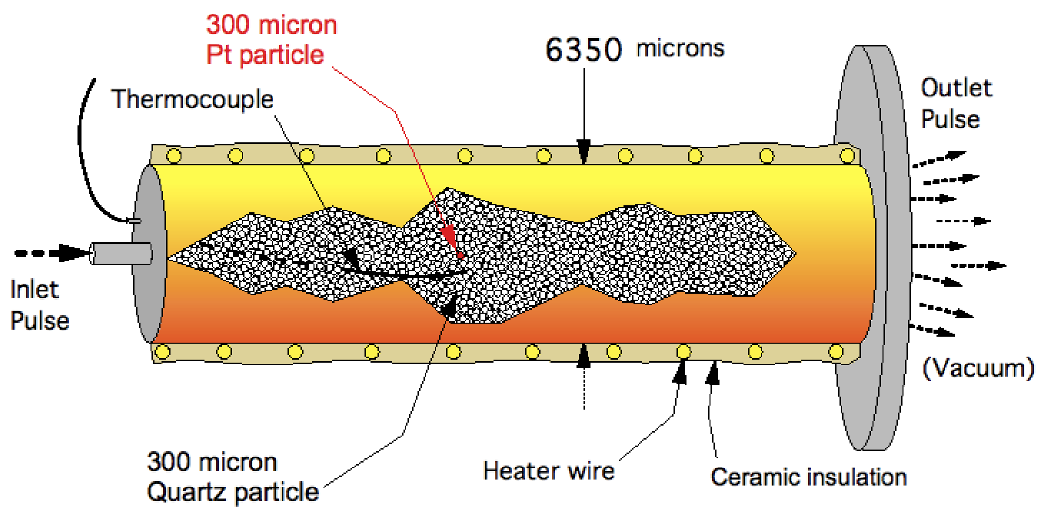
Non-uniformity along the catalyst bed was produced in multi-pulse experiment

Thin-zone and Single Particle Reactor Configurations

Thin-zone

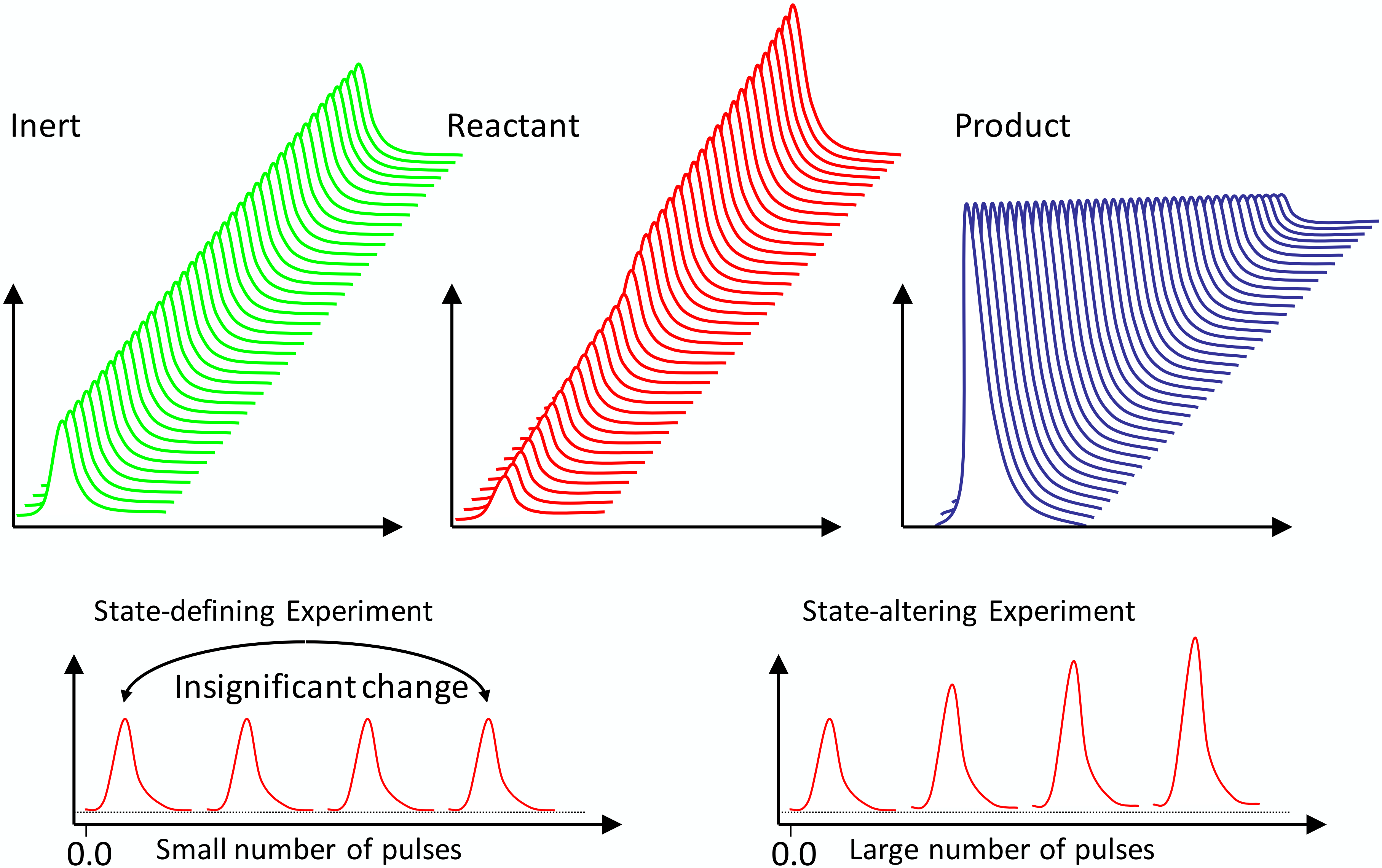


Single-particle



TAP Multipulse Experiment Combines

State-Defining & State-Altering Experiment



Principles of the TAP-experiment

- **3 principles**:
- (1) Insignificant change of catalyst composition during the single pulse
- (2) Controlled change of catalyst composition during the series of pulses
- (3) Uniformity of the active zone regarding the composition

=========

And… **Transport is well-defined**: Knudsen diffusion

- **Interrogative kinetics,** a systematic approach combining small stepwise changes in catalyst surface composition with precise kinetic characterization after each change to elucidate the evolution of catalyst properties and provide information on the relationship between surface composition and kinetic properties. (developed by J.T. Gleaves and G. Yablonsky in 1997)

Interrogative Kinetics (IK) Approach

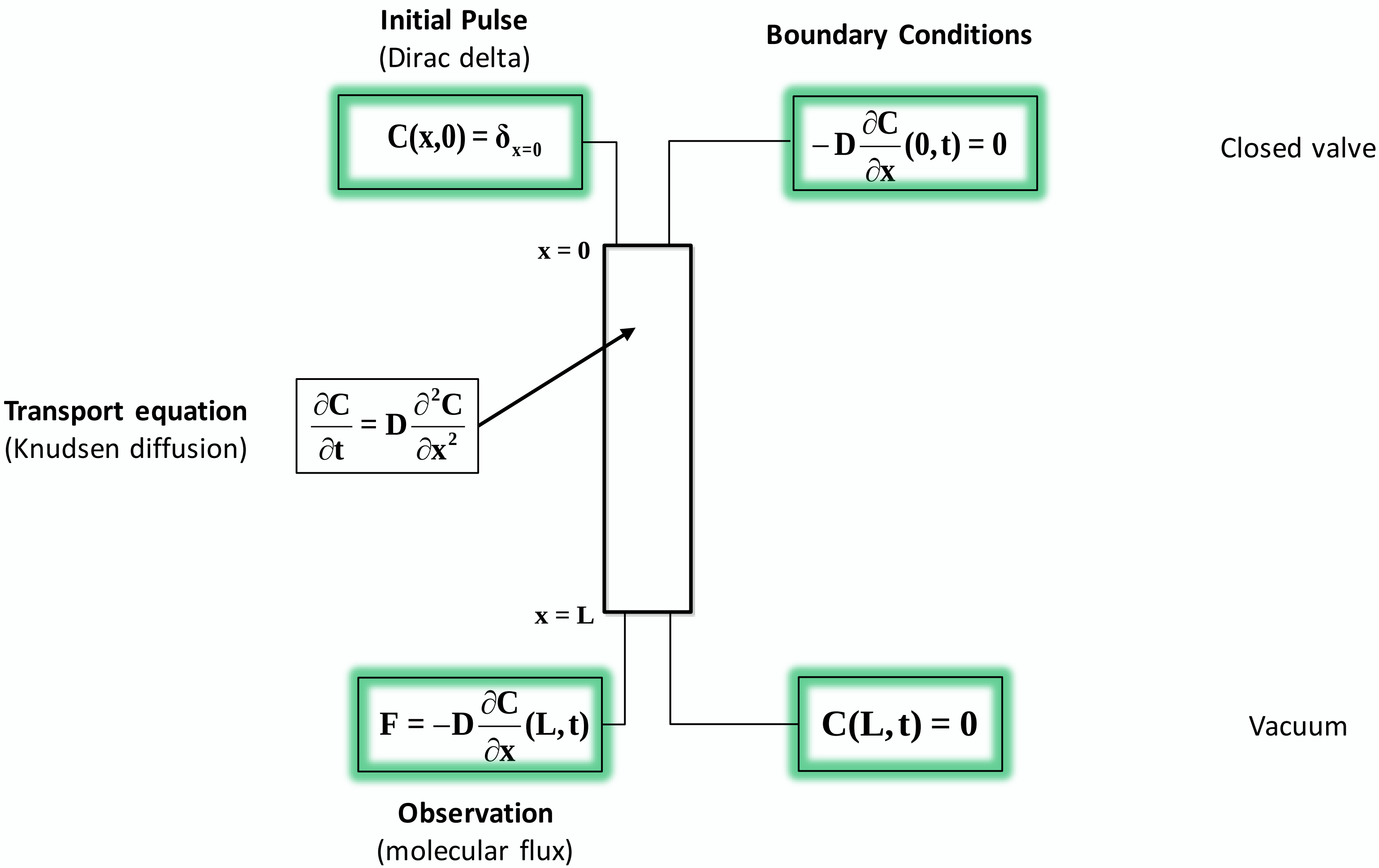
Was firstly introduced in the paper:
Gleaves, J.T., Yablonskii, G.S., Phanawadee, Ph., Schuurman, Y.
"TAP-2: An Interrogative Kinetics Approach" *Appl*. *Catal*., A: General, 160 (1997) 55.

The main idea is to combine two types of experiments:

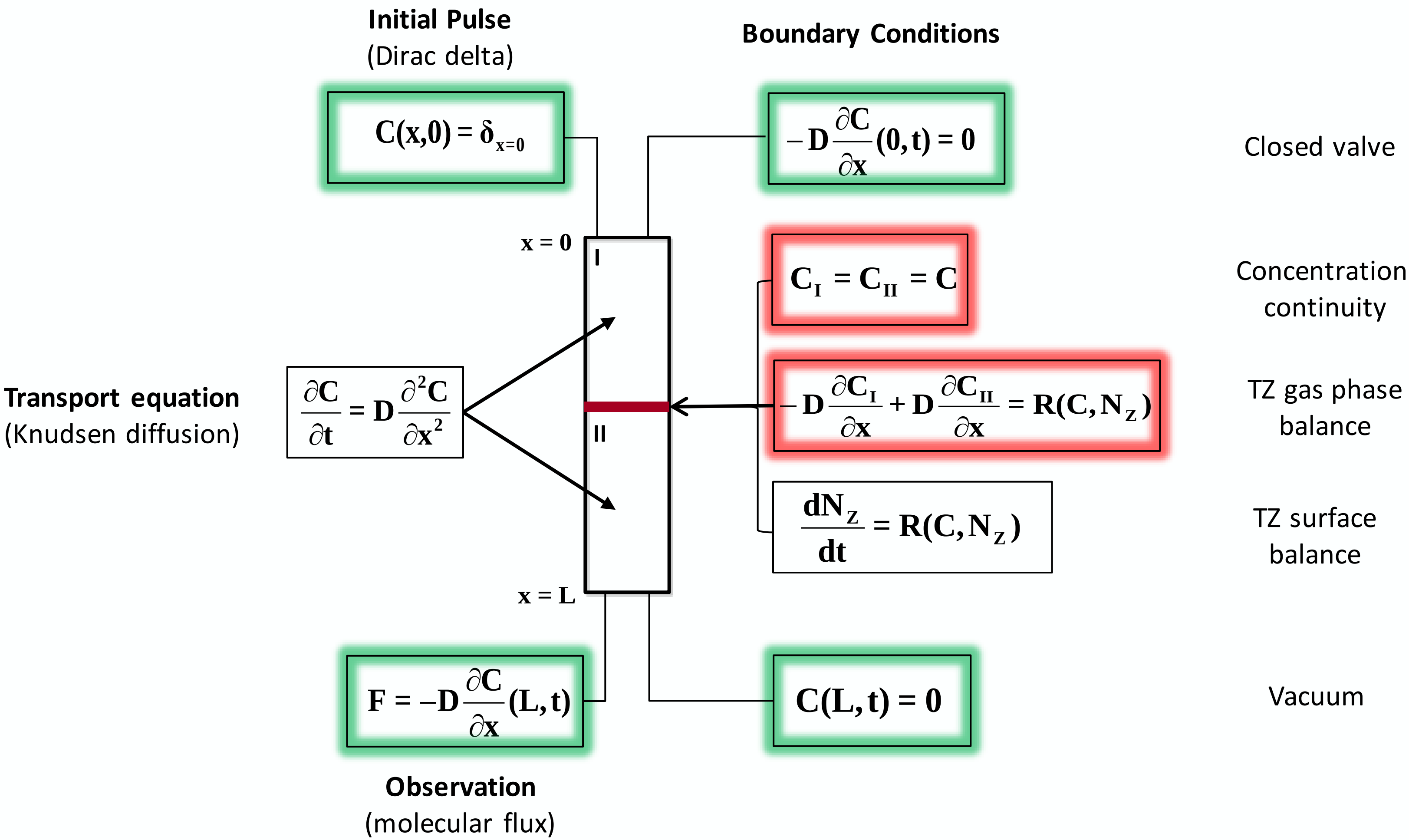
A state-defining experiment in which the catalyst composition and structure change insignificantly during a kinetic test

A state-altering experiment in which the catalyst composition is changed in a controlled manner

One zone: the diffusion equation requires an initial condition and two boundary conditions (as a second order PDE)



Two zones: each zone requires two boundary conditions



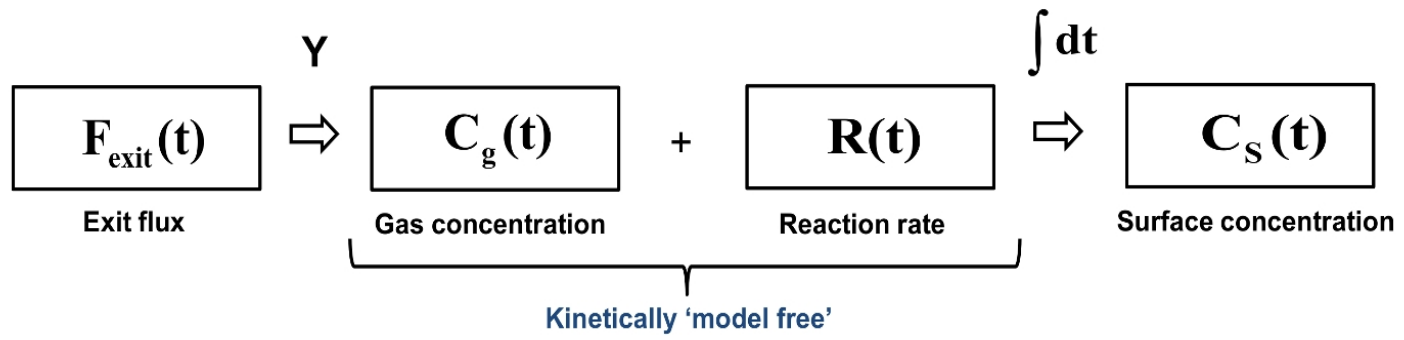
G. S. Yablonsky, D. Constales, et. al., *Chem. Eng. Sci.*, **62**, 6754 (2007)

Mathematical foundation of the Y-procedure:3 steps

- 1. exact solution in the Laplace domain;
- 2. switching to the Fourier domain to allow sufficient computation;
- 3. introduction to discretization and filtering in the Fourier domain to deal with the real data (in the time domain) subject to noise.

Transposition to the Fourier domain combined with time discretization and filtering of the high-frequency noise leads to an efficient practical method for the reconstruction of gas-phase concentrations in a non-steady-state regime without any presuppositions about the kinetic dependence, that is, it is a model-free procedure.

The Y-Procedure analysis provides us with:

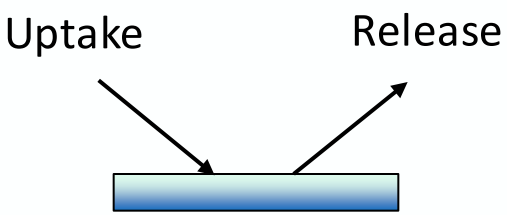


- 'Model free' transient kinetics
- Millisecond time resolution
- For complex multicomponent catalysts
- At the upper limit of the surface science range (10^{-6} torr)
- Keeping high spacial uniformity for conversions up to 80% [1]

How do we deal with this information?

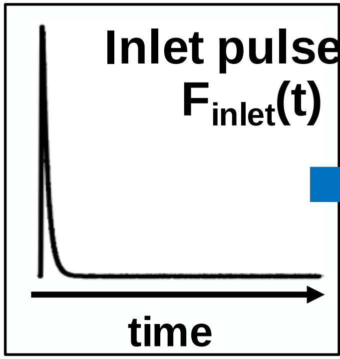
[1] - S. Shekhtman, et. al., *Chem. Eng. Sci.*, **59**, 5493 (2004)

Calculating surface concentrations (instantaneous storages) as a transient difference between total uptake and release

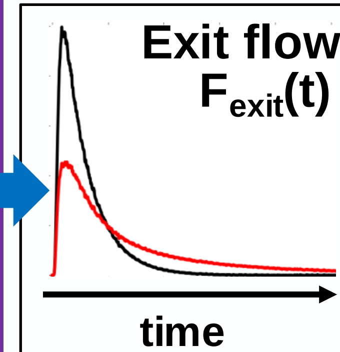


$$\mathbf{C_S(t) = Uptake(t) - Release(t) = \int_0^t \sum_i \nu_i R_i(\tau) d\tau}$$

Thin-Zone (TZ) Temporal Analysis of Products (TAP)



Virtual TZ TAP experiments with **realistic noise model**



Y-Proc.

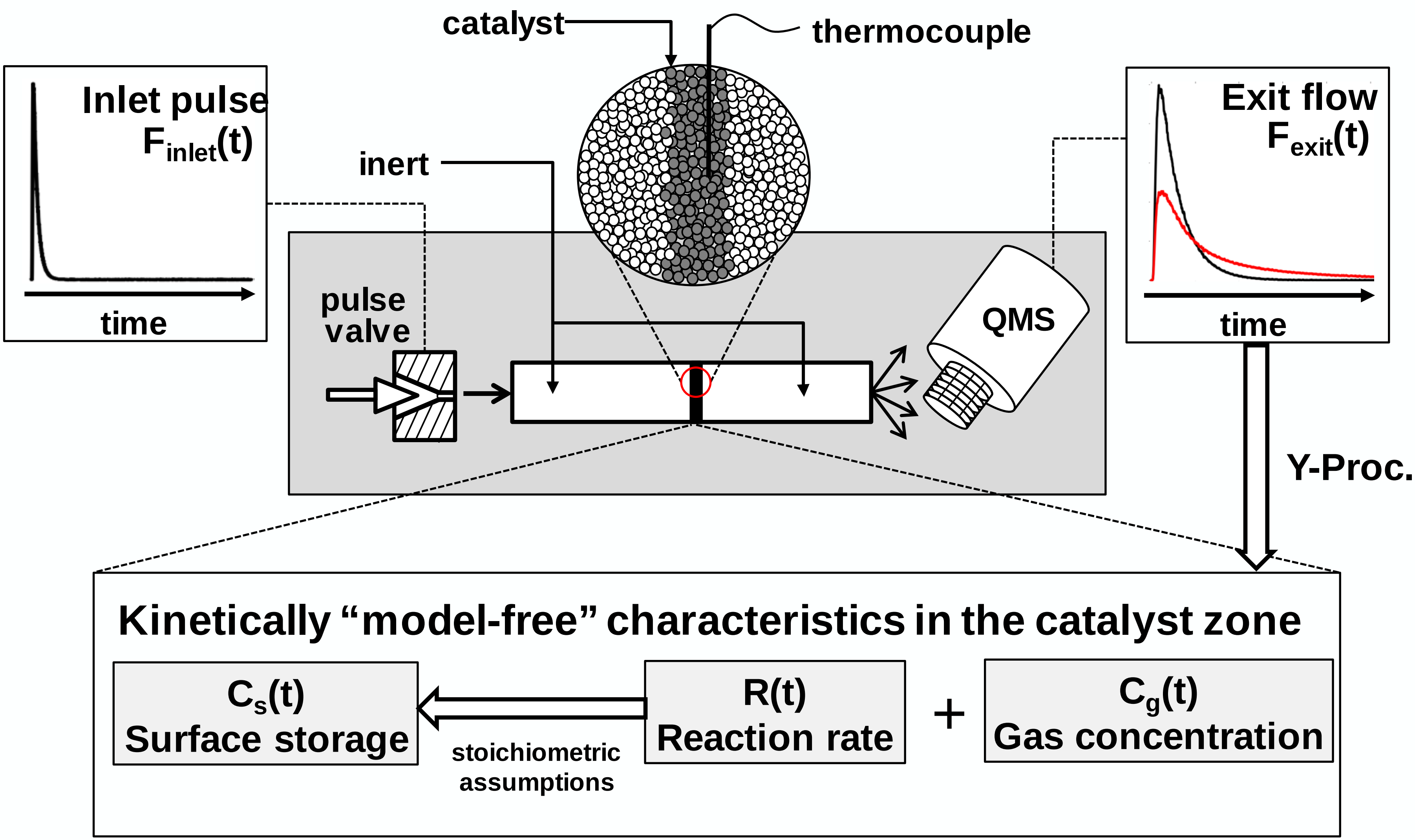
Kinetically "model-free" characteristics in the catalyst zone

$C_s(t)$ Surface storage ⇐ **stoichiometric assumptions** ⇐ **$R(t)$ Reaction rate** + **$C_g(t)$ Gas concentration**

$$C_{ZCO}(t) = C_{ZCO,init} + \int_0^t R_{CO}(t')dt' - \int_0^t R_{CO_2}(t')dt'$$

$$C_{ZO}(t) = C_{ZO,init} + \int_0^t 2R_{O_2}(t')dt' - \int_0^t R_{CO_2}(t')dt'$$

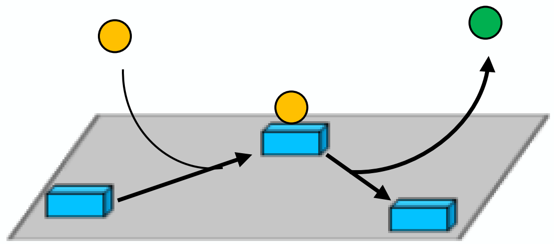
Thin-Zone (TZ) Temporal Analysis of Products (TAP)



G. S. Yablonsky et al. (2007)

Communication between gas and surface phases

1



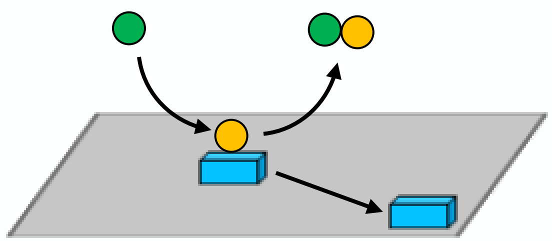
- surface site Z
- gas molecule A or B

Molecular adsorption: Z + A = ZA

Dissociative adsorption: 2Z + A = 2ZA

Product release: ZA = Z + B

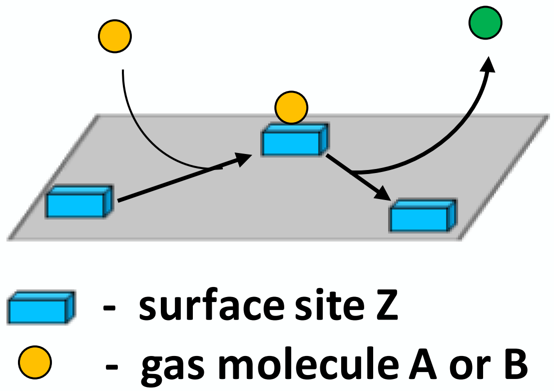
2



Impact reaction steps: ZA + B = Z + AB

Communication between gas and surface phases

1

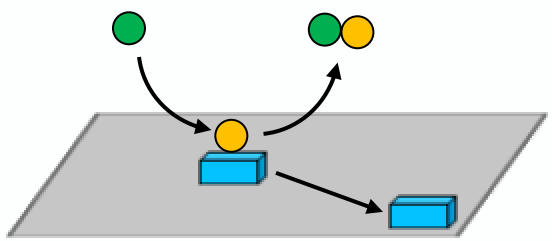


Molecular adsorption: $Z + A = ZA$

Dissociative adsorption: $2Z + A = 2ZA$

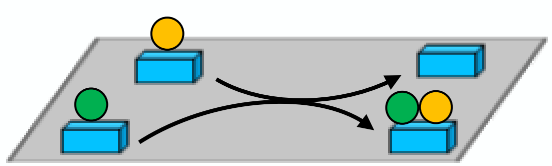
Product release: $ZA = Z + B$

2



Impact reaction steps: $ZA + B = Z + AB$

3



'Hidden' surface steps:

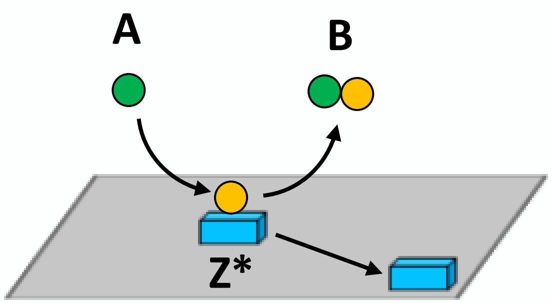
$ZA + ZB = Z + ZC$

$ZA = ZC$

$ZA + Z = Z_2A$

Testing kinetic coherency

Kinetic coherency – Every combination of elementary steps leads to synchronization of certain kinetic characteristics



Rate-Rate coherency:

If A is consumed and B is produced in the same step, their rates must be synchronized (equal in this case):

$$R_A(t) = R_B(t)$$

Rate-Concentration coherency:

Assuming the law of mass actions is valid, certain combinations of rates and concentrations must be synchronized, e.g:

$$R_{AB}(t) \,/\, C_A(t)C_{Z*}(t) \neq f(t)$$

Case study model: CO oxidation

Elementary steps:

(1) $O_2 + 2Z \rightarrow 2ZO$

(2) $CO + Z \leftrightarrow ZCO$

(3) $CO + ZO \rightarrow Z + CO_2$

(4) $ZCO + ZO \rightarrow 2Z + CO_2$

(5) $ZO + Z_b \rightarrow Z + Z_bO$

Case study model: CO oxidation

Eley-Rideal (ER):

(1) $O_2 + 2Z \rightarrow 2ZO$

(2) $CO + Z \leftrightarrow ZCO$

(3) $CO + ZO \rightarrow Z + CO_2$

(4) $ZCO + ZO \rightarrow 2Z + CO_2$

(5) $ZO + Z_b \rightarrow Z + Z_bO$

Case study model: CO oxidation

Langmuir-Hinshelwood (LH):

(1) $O_2 + 2Z \rightarrow 2ZO$

(2) $CO + Z \leftrightarrow ZCO$

(3) $CO + ZO \rightarrow Z + CO_2$

(4) $ZCO + ZO \rightarrow 2Z + CO_2$

(5) $ZO + Z_b \rightarrow Z + Z_bO$

Combined (ER+LH):

(1) $O_2 + 2Z \rightarrow 2ZO$

(2) $CO + Z \leftrightarrow ZCO$

(3) $CO + ZO \rightarrow Z + CO_2$

(4) $ZCO + ZO \rightarrow 2Z + CO_2$

(5) $ZO + Z_b \rightarrow Z + Z_bO$

Case study model: CO oxidation

Buffer Step (ER+BS):

(1) $O_2 + 2Z \rightarrow 2ZO$

(2) $CO + Z \leftrightarrow ZCO$

(3) $CO + ZO \rightarrow Z + CO_2$

(4) $ZCO + ZO \rightarrow 2Z + CO_2$

(5) $ZO + Z_b \rightarrow Z + Z_bO$

Case study model: CO oxidation

Additional Oxygen Process (ER+AOP):

(1) $O_2 + 2Z \rightarrow 2ZO$

(2) $CO + Z \leftrightarrow ZCO$

(3) $CO + ZO \rightarrow Z + CO_2$

(4) $ZCO + ZO \rightarrow 2Z + CO_2$

(5) $ZO + Z_b \rightarrow Z + Z_bO$

Case study model: CO oxidation

Elementary steps:

(1) $O_2 + 2Z \rightarrow 2ZO$

(2) $CO + Z \leftrightarrow ZCO$

(3) $CO + ZO \rightarrow Z + CO_2$

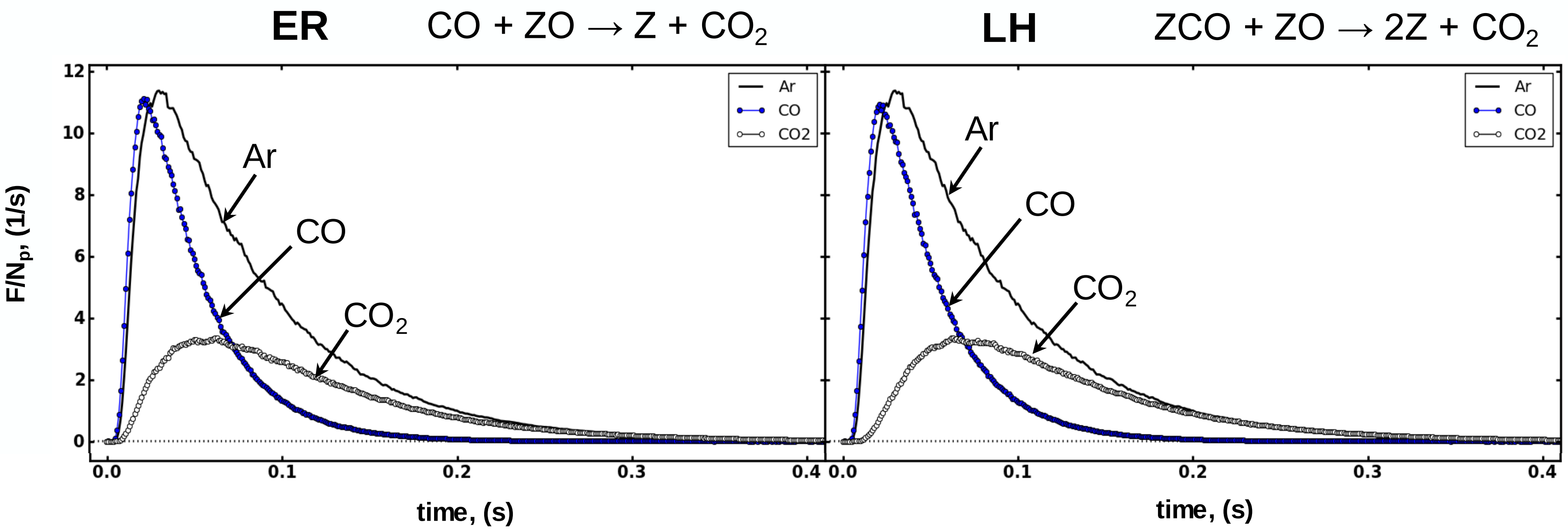
(4) $ZCO + ZO \rightarrow 2Z + CO_2$

(5) $ZO + Z_b \rightarrow Z + Z_bO$

Possible mechanisms:

[1] ER
[2] LH
[3] ER+LH
[4] ER+BS
[5] ER+AOP
[6] LH+AOP
[7] ER+BS+AOP
[8] ER+LH+AOP

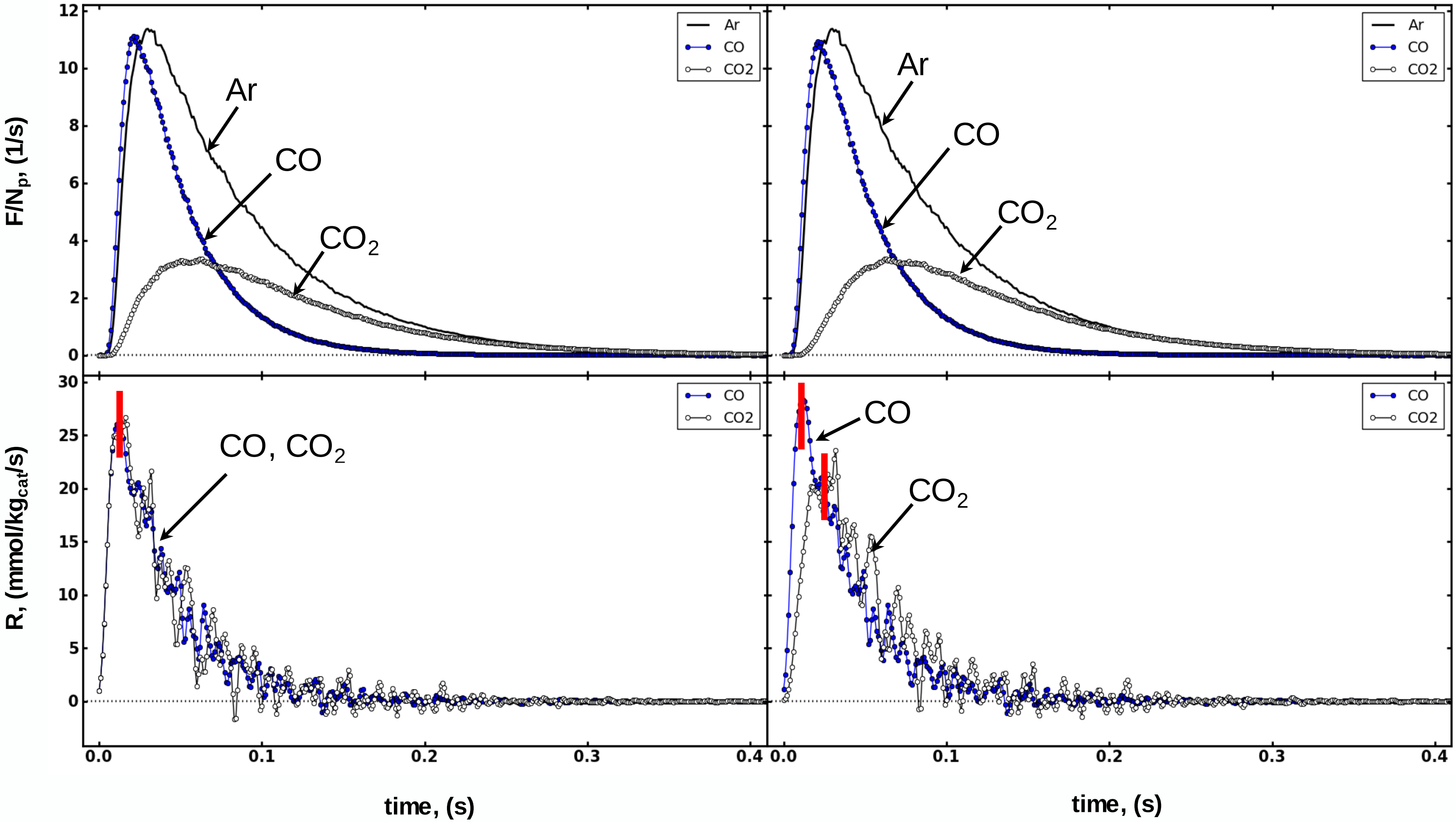
Rate-Rate coherency



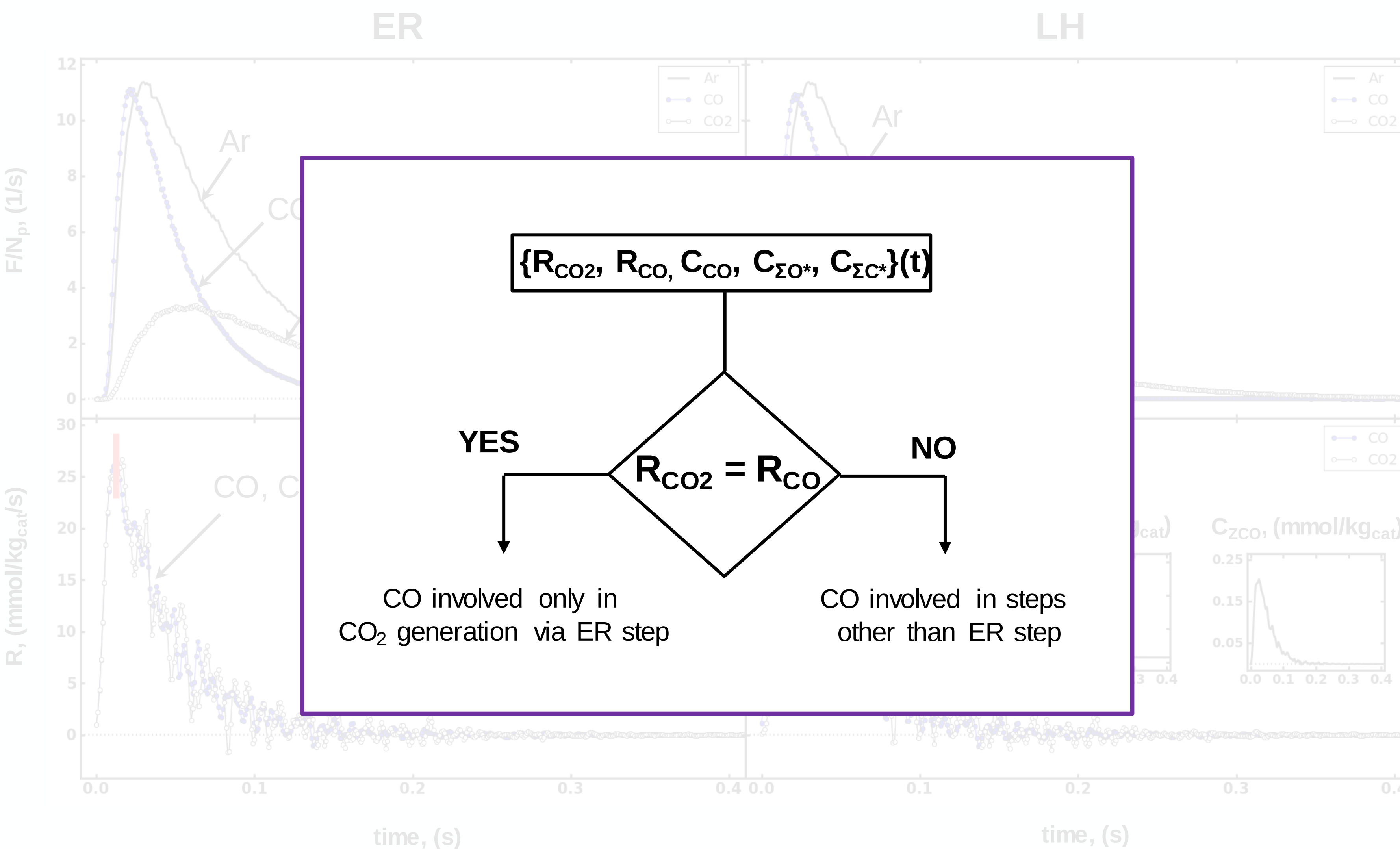
Rate-Rate coherency

ER $CO + ZO \rightarrow Z + CO_2$

LH $ZCO + ZO \rightarrow 2Z + CO_2$



Rate-Rate coherency



Rate-Concentration coherency

Is CO_2 formed **only** through ER step or(also) through LH steps?

ER, ER+BS: $R_{CO_2} = k^{ER} C_{ZO} C_{CO}$

Rate-Concentration coherency

Is CO_2 formed **only** through ER step or(also) through LH steps?

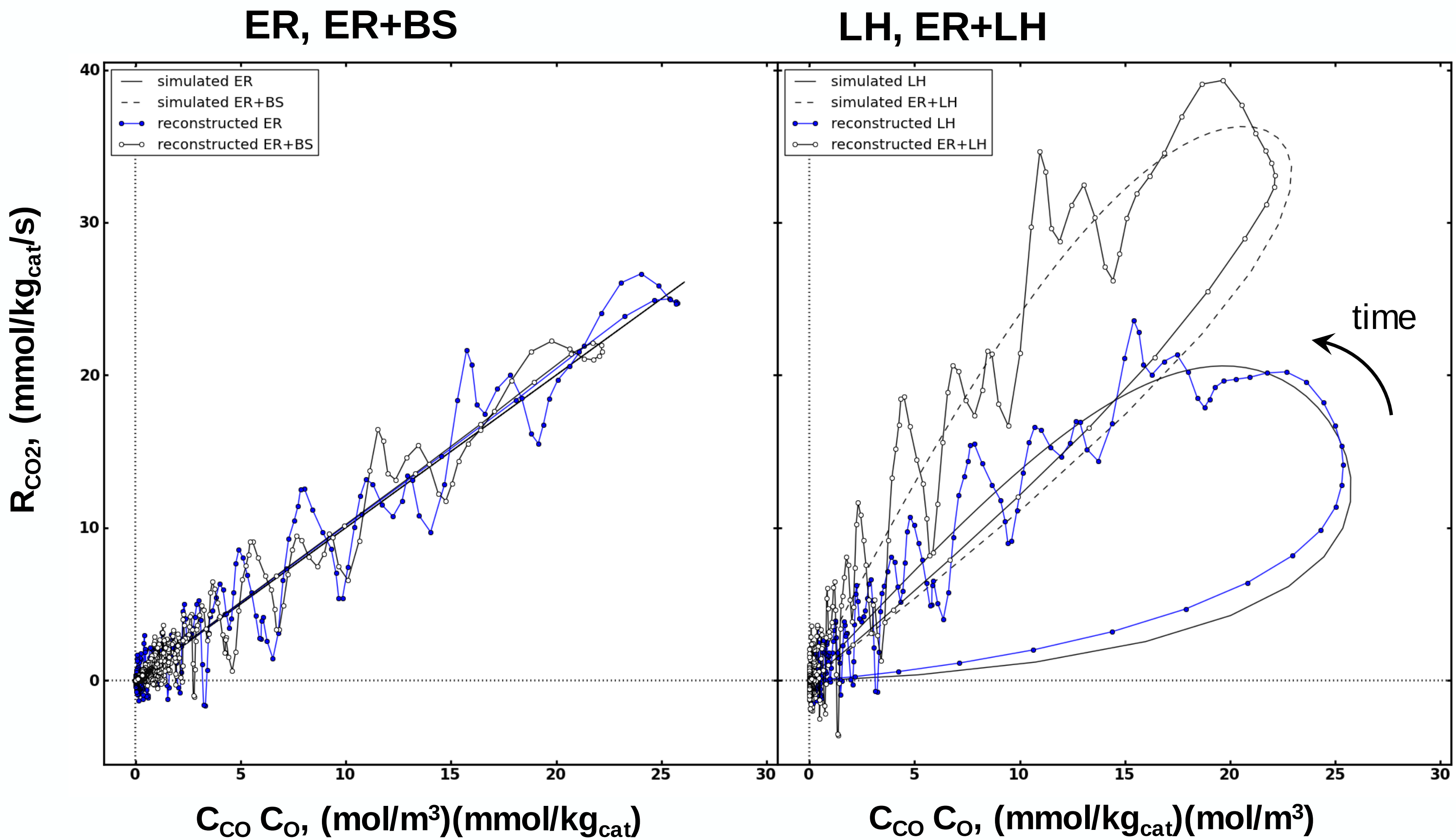
ER, ER+BS:

$$R_{CO_2} = k^{ER} C_{ZO} C_{CO}$$

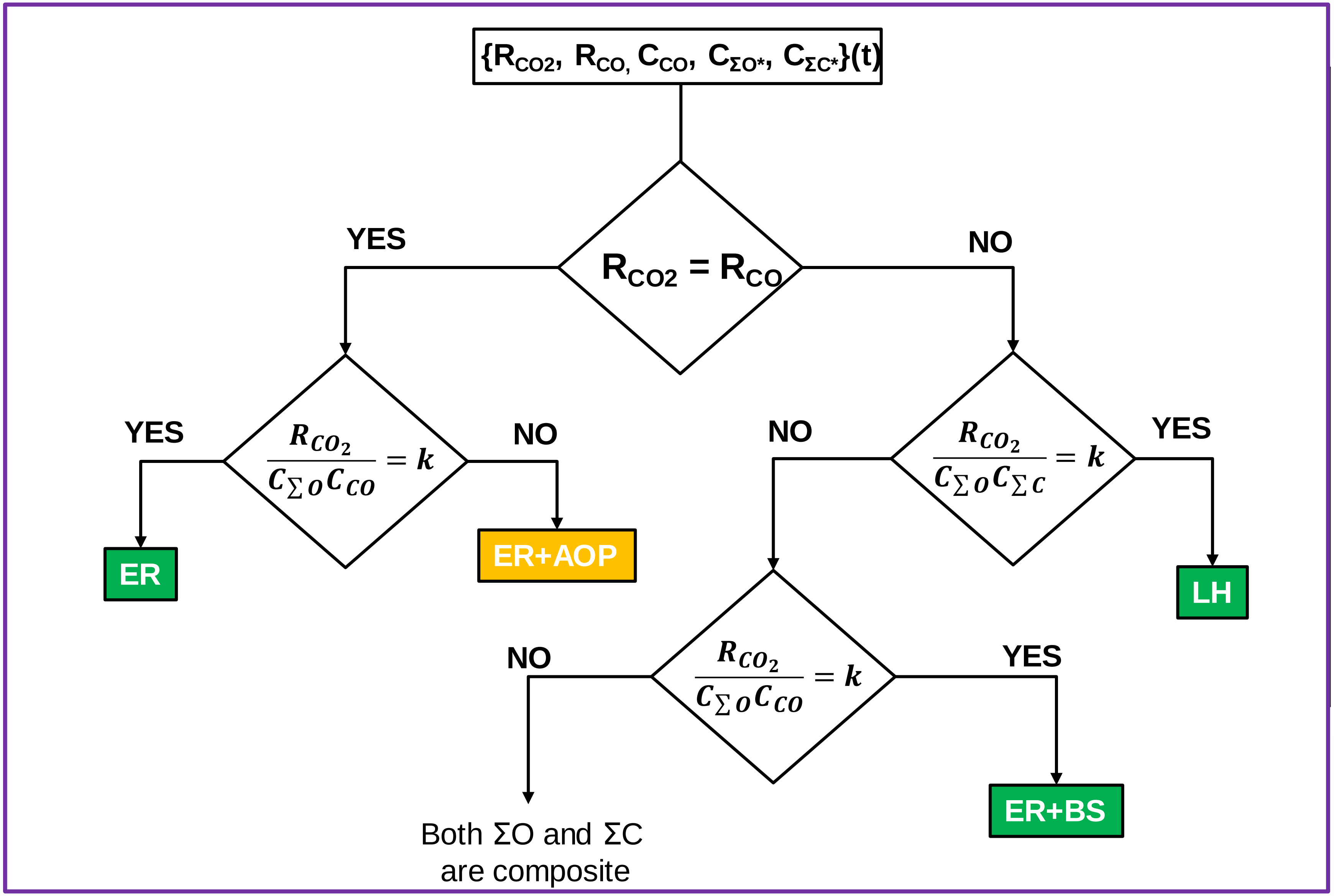
Data should give a **linear plot** in these coordinates …

… unless other steps are involved.

Rate-Concentration coherency



Rate-Concentration coherency



Rate-Concentration coherency

Is CO_2 formed **only** through a combined ER+LH mechanism or other processes are also involved?

ER+LH: $$R_{CO_2} = k^{ER} C_{ZO} C_{CO} + k^{LH} C_{ZO} C_{ZCO}$$

Rate-Concentration coherency

Is CO_2 formed **only** through a combined ER+LH mechanism or other processes are also involved?

ER+LH: $$R_{CO_2} = k^{ER} C_{ZO} C_{CO} + k^{LH} C_{ZO} C_{ZCO}$$

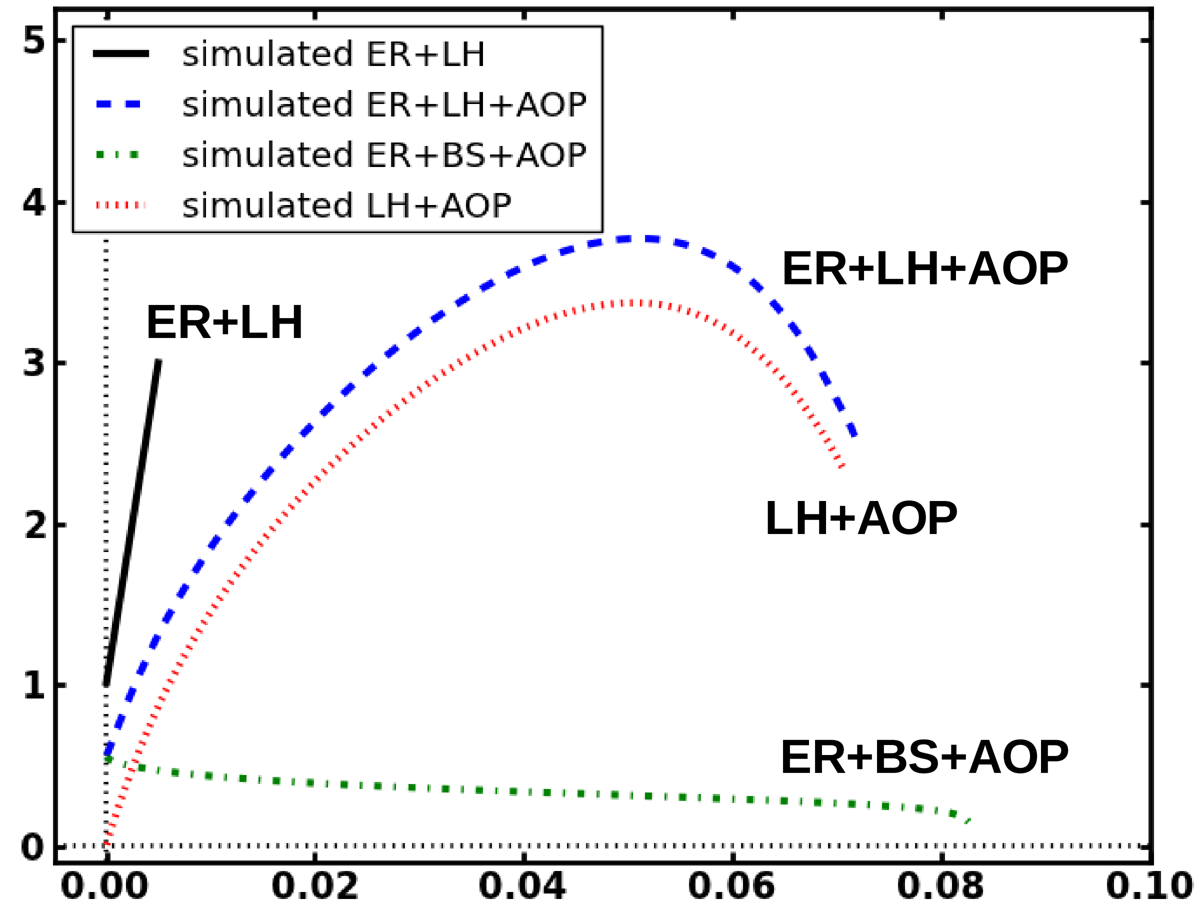
$$\boxed{\frac{R_{CO_2}}{C_{ZO} C_{CO}}} = k^{ER} + k^{LH} \boxed{\frac{C_{ZCO}}{C_{CO}}}$$

Data should give a **linear plot** in these coordinates …

… unless other steps are involved.

Rate-Concentration coherency

$$\frac{R_{CO_2}}{C_{\sum O} C_{CO}}, \left(\frac{m^3}{s \cdot mol}\right)$$

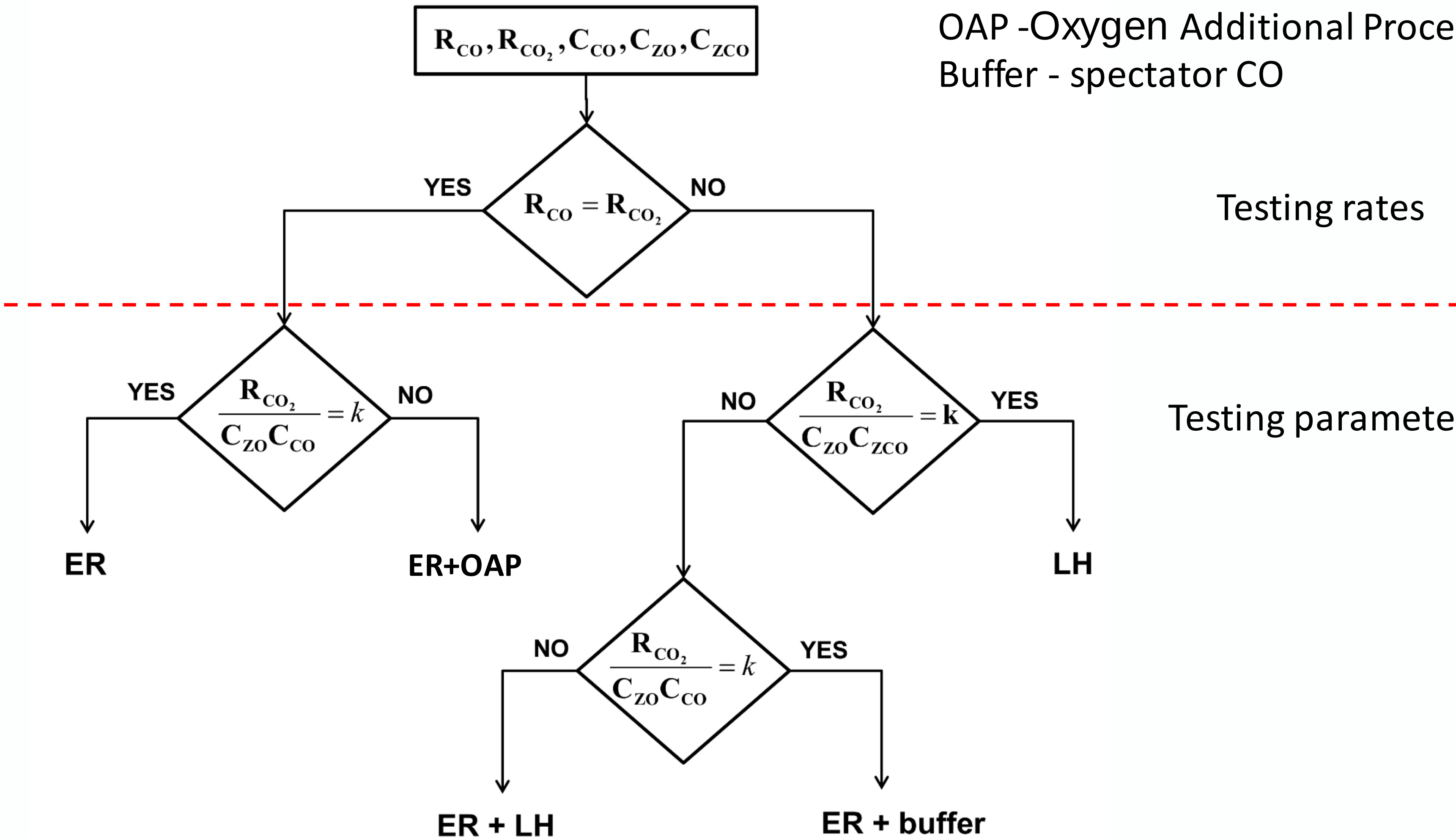


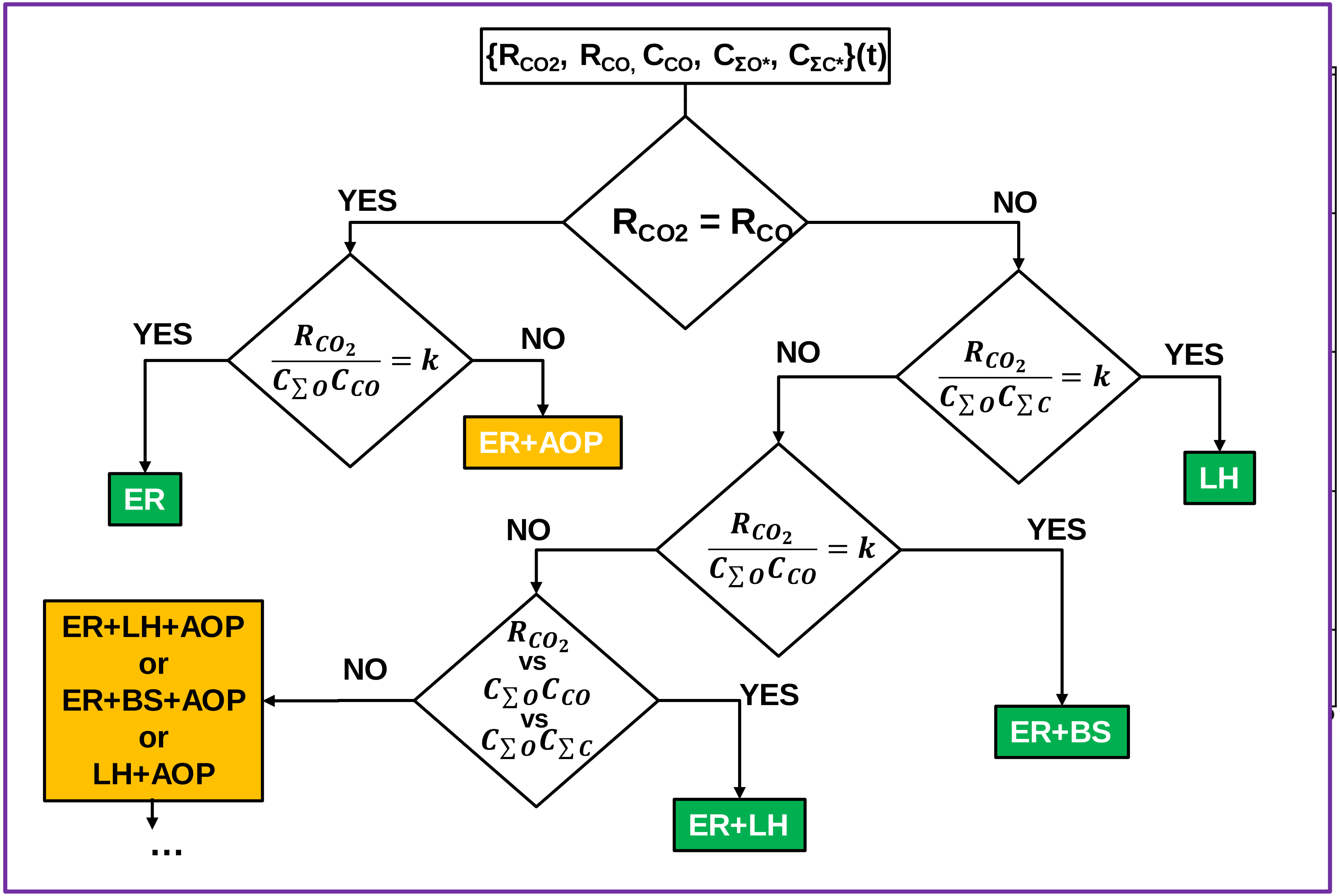
$$\frac{C_{\sum C}}{C_{CO}}, \left(\frac{m^3}{kg_{cat}}\right)$$

Decision tree in determining mechanisms for oxygen pre-covered surface

Legend:

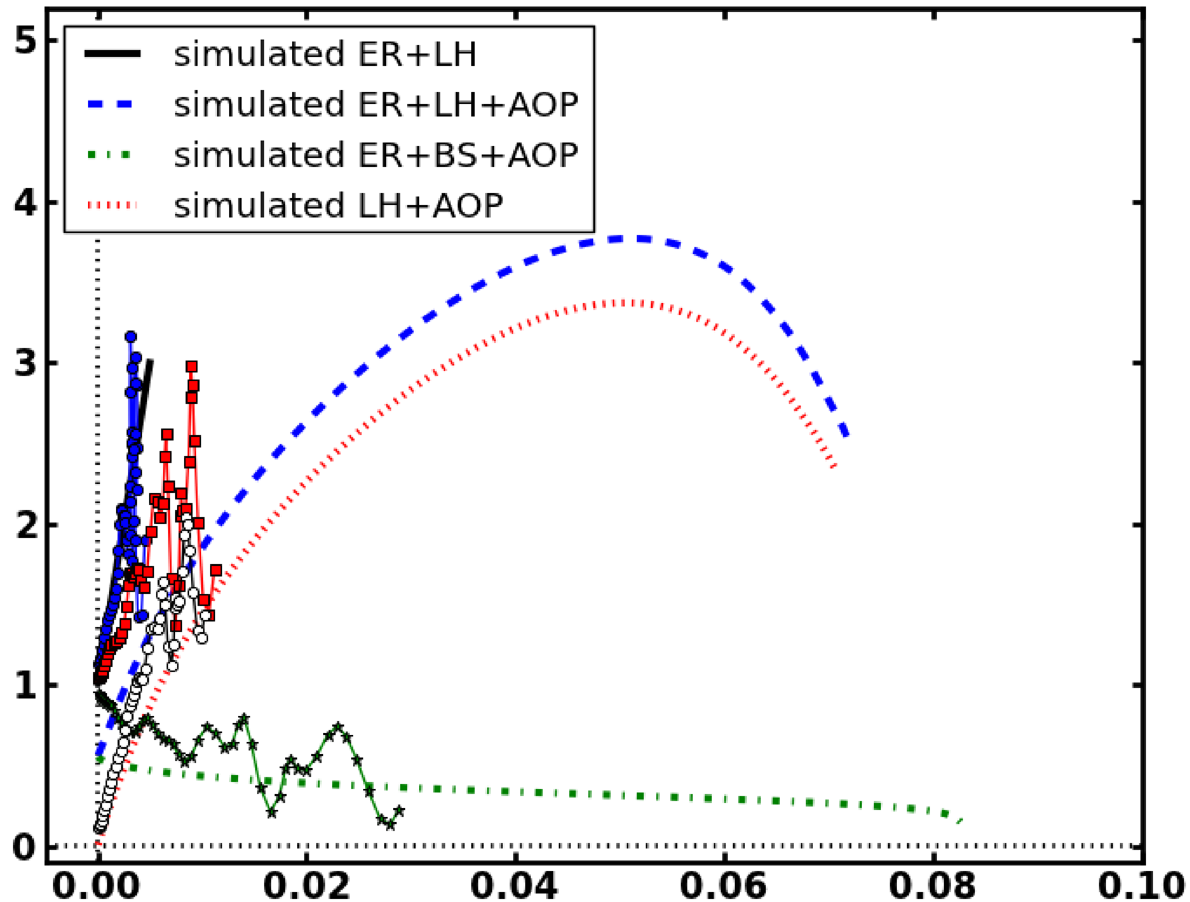
ER - Eley-Rideal
LH - Langmuir-Hinshelwood
OAP -Oxygen Additional Process
Buffer - spectator CO




{RCO2, RCO, CCO, CΣO*, CΣC*}(t)
RCO2 = RCO
YES
NO
$\frac{R_{CO_2}}{C_{\sum O} C_{CO}} = k$
YES
NO
ER
ER+AOP
$\frac{R_{CO_2}}{C_{\sum O} C_{\sum C}} = k$
NO
YES
LH
$\frac{R_{CO_2}}{C_{\sum O} C_{CO}} = k$
NO
YES
ER+BS
R_{CO_2} vs $C_{\sum O} C_{CO}$ vs $C_{\sum O} C_{\sum C}$
NO
YES
ER+LH+AOP or ER+BS+AOP or LH+AOP
ER+LH
...

Noise challenge

$$\frac{R_{CO_2}}{C_{\sum O} C_{CO}}, \left(\frac{m^3}{s \cdot mol}\right)$$



$$\frac{C_{\sum C}}{C_{CO}}, \left(\frac{m^3}{kg_{cat}}\right)$$

"Stop time, thou art so beautiful!“

(“Faust”, Goethe)

Goethe, “Faust”

“Werd ich zum Augenblicke sagen:
Verweile doch: du bist zu schoen

Dann magst du mich in Fesseln schlagen,

Dann will ich gern zugrude gehn”.

Difference from the Faust's strategy

In chemical time studies, we would like to stop any moment of time, not just the beautiful one.

TAP-results

- **About 20 machines working in the world**
- **About 10 research groups**

US-St. Louis, Houston

Europe – Belgium, Ghent;

Netherlands, Delft ; N. Ireland, UK, Belfast;

Germany – Ulm, Rostock, Bohum;

France –Lyon; Spain; Switzerland –Zuerich;

Asia- Japan – Tokyo, Toyota City;

Thailand – Bangkok.

Many catalytic reactions: oxidation of simple molecules, many reactions of complete and selective oxidation of hydrocarbons

Conclusions

(1) Within the Chemical Calculus approach, we have presented a novel strategy for **discriminating between minimal catalytic mechanisms** from a pool of all possible elementary steps.

(2) There was developed an experimental method of testing the non-steady-state catalytic reaction using the method of insignificant perturbations (TAP-pulse response method using the thin-zone reactor

.

.

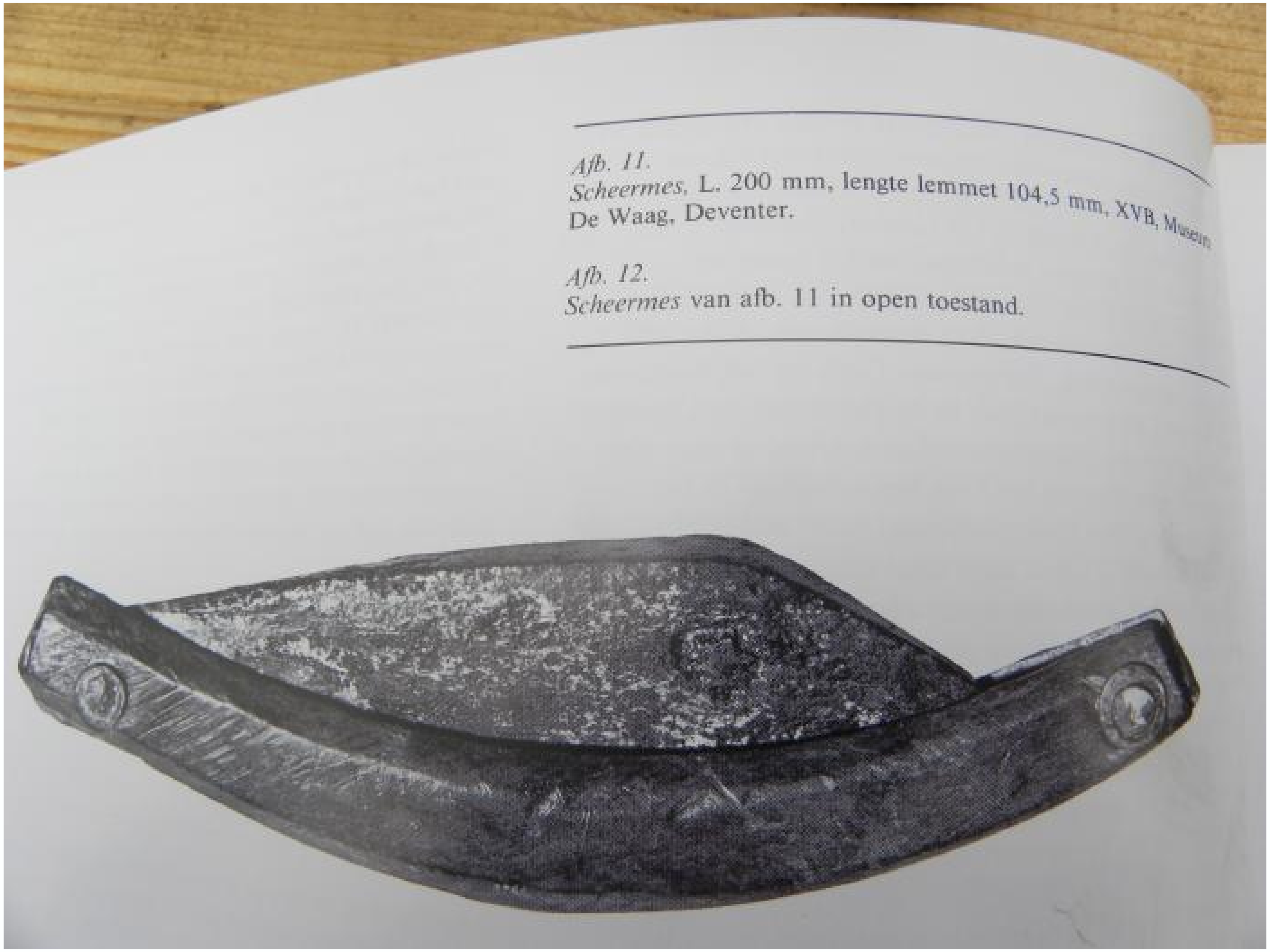
(3**)** There was developed a special procedure for extracting Rate, Concentrations and "Storages" of the non-steady-state catalyst..

(4) Testing the "rate-rate" and "rate-concentration" coherency is used for distinguishing the detailed mechanisms

Pomona, the Roman Goddess of Fruitful Abundance

William of Occam (1288-1348)

Occam's razor



Occam's Razor

Entia non sunt multiplicanda praeter necessitatem

(entities must not be multiplied beyond necessity)

- These words attributed to Ockham are absent in his extant works

Origami Bonsai Tree as a Ideal Scientific Model

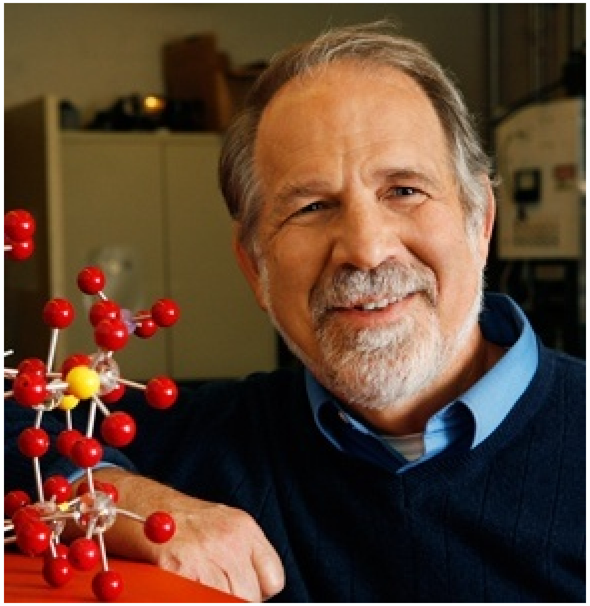
Final step of modeling

“It has seen further it is by standing on the shoulders of giants”

(Isaac Newton,

Letter to Robert Hook, February 1676)

Prof. John T. Gleaves



Prof. Alexander Gorban

Gregory S. Yablonsky

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