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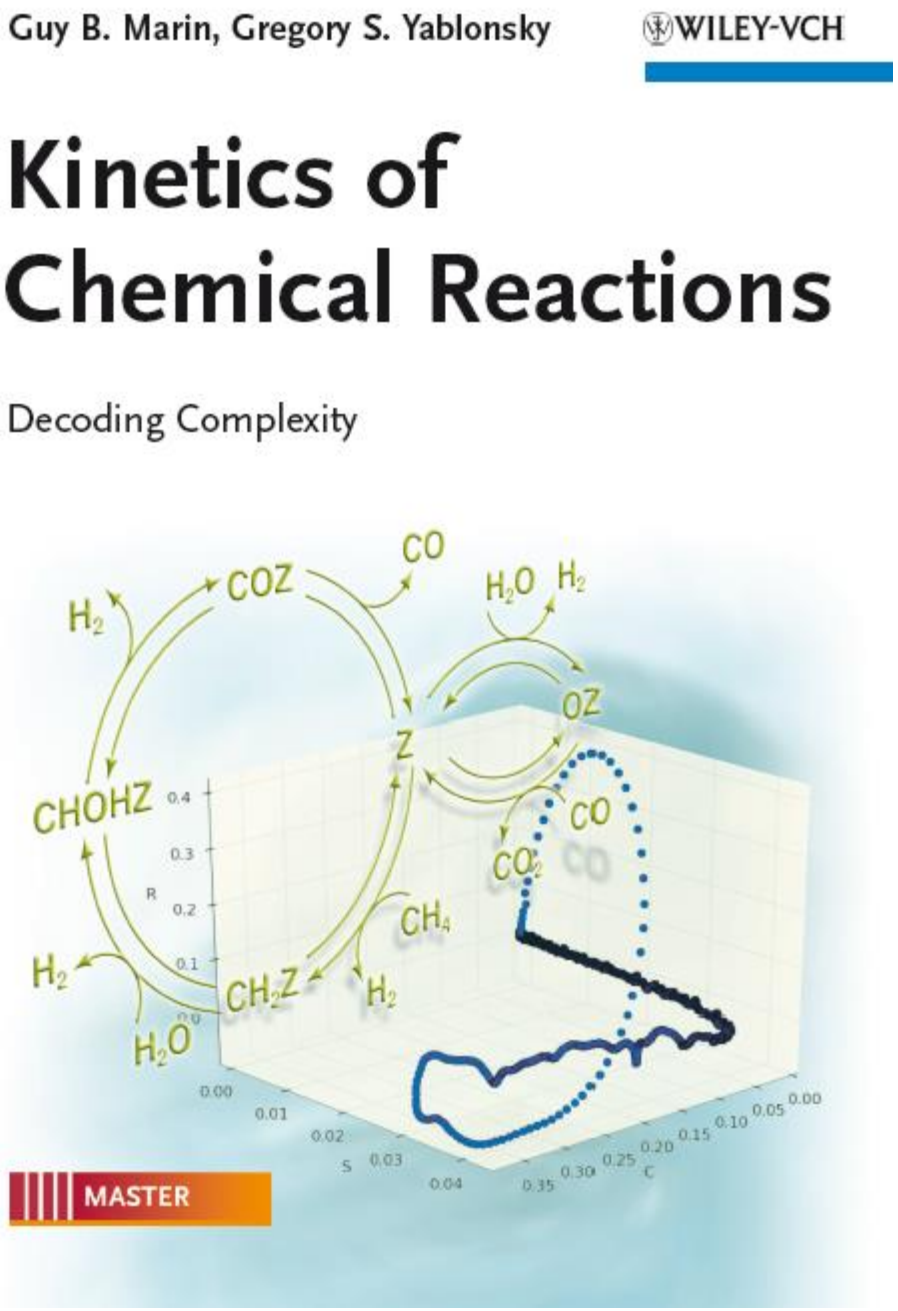


Guy B. Marin, Gregory S. Yablonsky

WILEY-VCH

Kinetics of Chemical Reactions

Decoding Complexity

MASTER

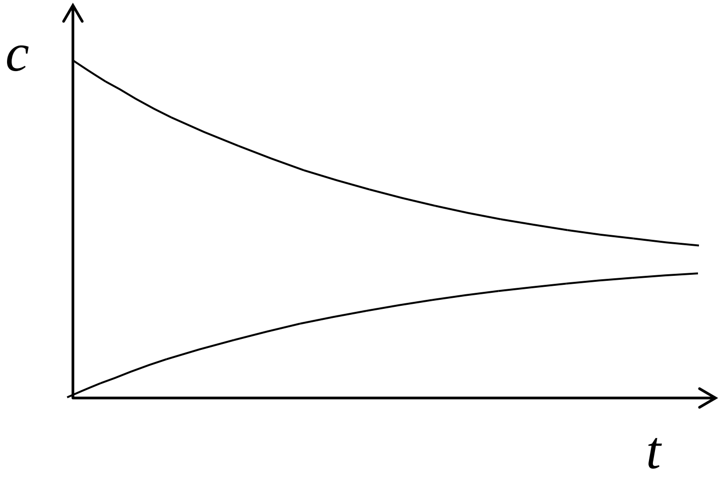
- **Joint Kinetics is a New Kinetic Strategy for Chemical Kinetics and Heterogeneous Catalysis**

- TRENDS AND EVENTS

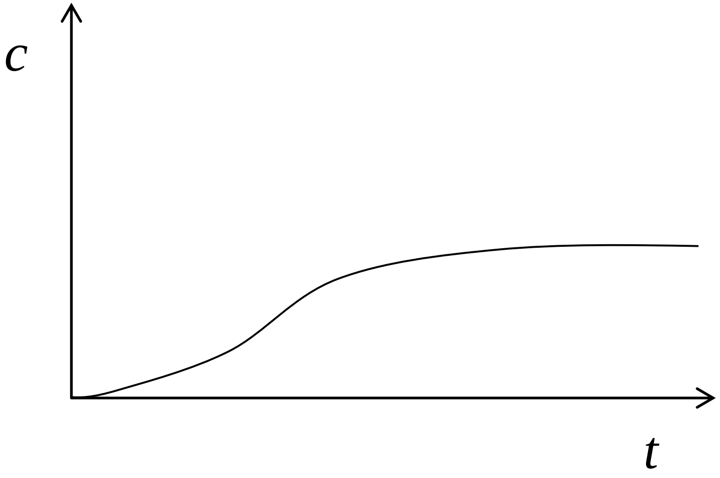
- TRENDS

# Types of Temporal Evolution – Relaxation

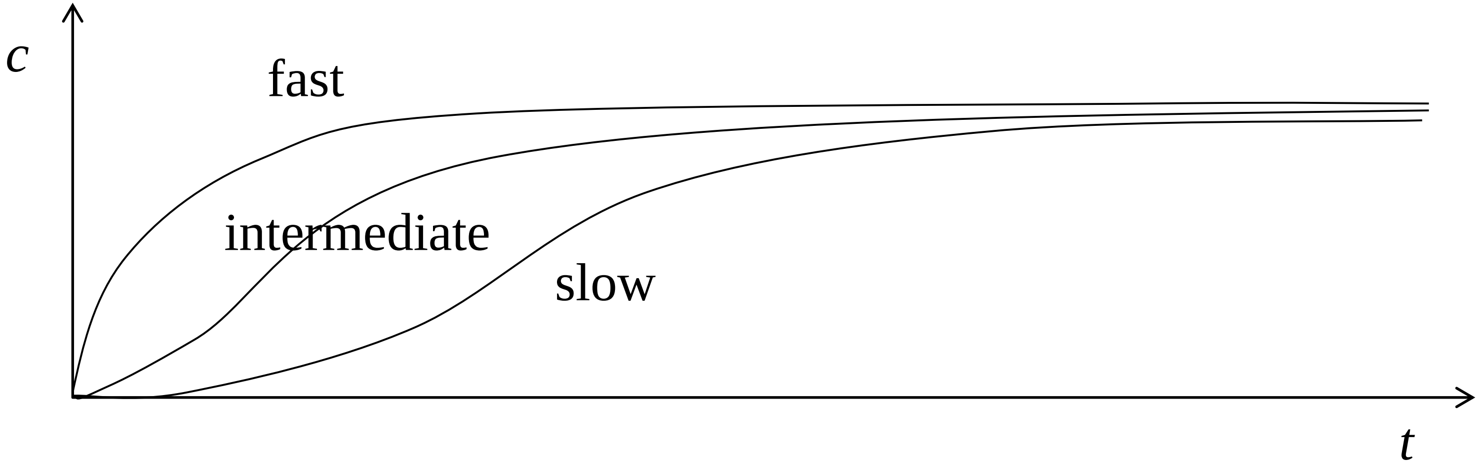
## Simple exponential relaxation



## Relaxation with induction period

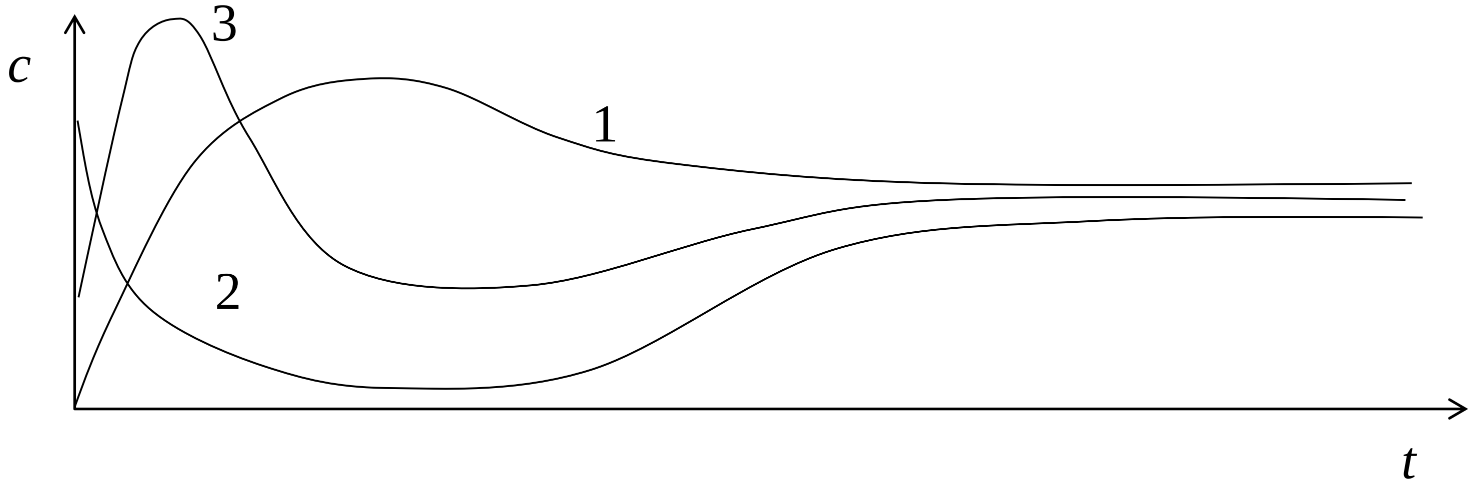


## Relaxation of different components at different time scales



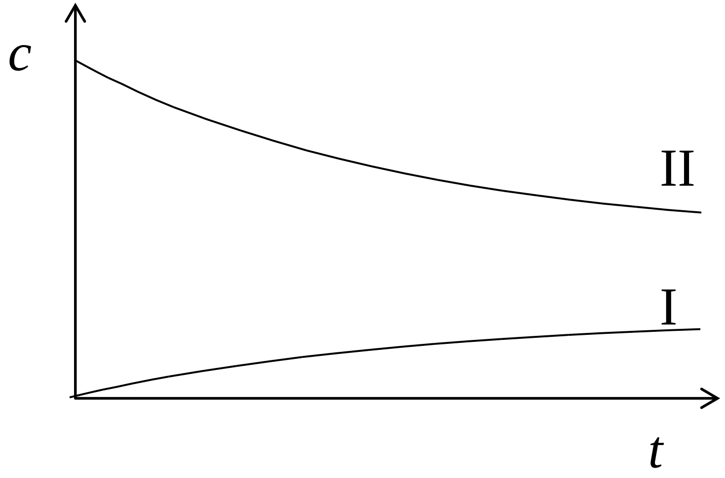
# Types of Temporal Evolution – Relaxation

Relaxation with “overshoots” (1) & (3) and start in “wrong” direction (2)

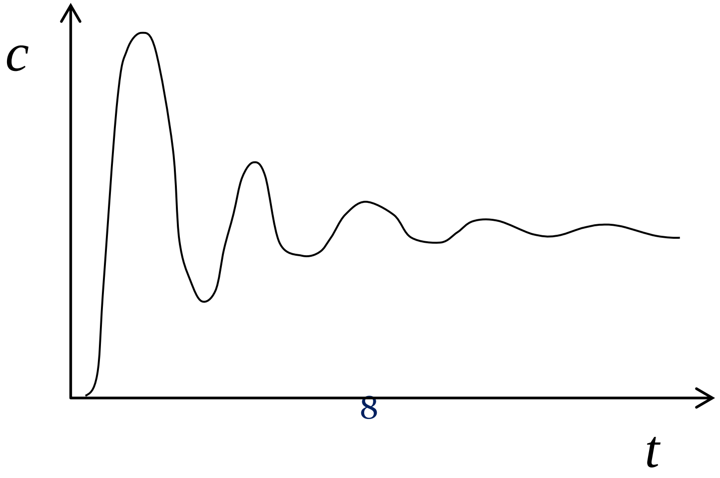


# Types of Temporal Evolution – Relaxation

Relaxation with different steady states

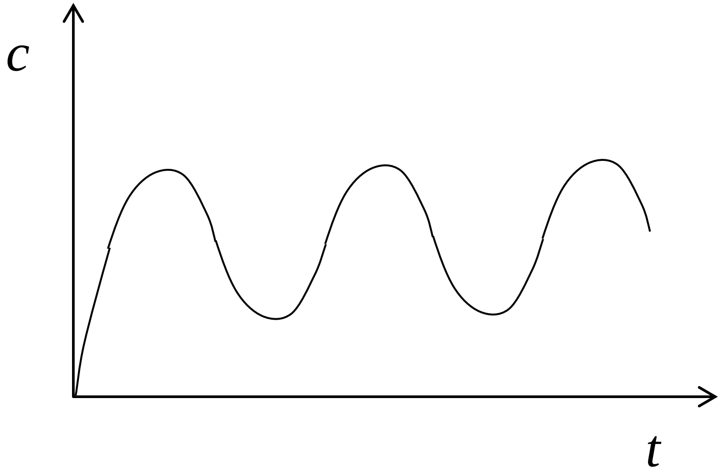


Damped oscillations

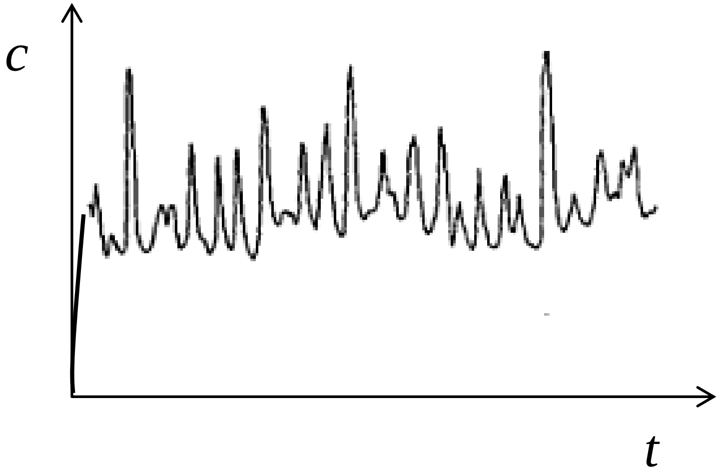


# Types of Temporal Evolution – Relaxation

Regular oscillations around a steady state



Chaotic oscillations



# Coherency in Trends

- Stoichiometry
- Symmetrical Invariants etc

# EVENTS

- Extremum (Maximum, Minimum)
- Turning Point
- Extinction
- Ignition
- Intersection of kinetic dependences
- Coincidence of events

etc….

# CATEGORIZATION of EVENTS

- “ALWAYS” (Unavoidable)
- “NEVER”
- “SOMETIMES” (Avoidable)

- **SIMPLE is COMPLEX**

# What is Joint Kinetics?

It is defined as the “trends-events’ analysis , i.e. the analysis of special combinations of kinetic dependences and events (intersections, coincidences etc).

A map of kinetic events is constructed and analyzed.

# MAIN TOPICS

I. Symmetrical Relations

II. Intersections and Coincidences

III. Kinetic and Thermodynamic Control

IV. Momentary Equilibrium

# I.

# Joint Kinetics: Symmetric Relations

# General Contemporary Dogma

**It is impossible to predict the temporal evolution of a reacting chemical system based on its description under equilibrium conditions**

# New Result: Reversible Linear Reactions

Batch reactor, $A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B$

- $(A_A(t), B_A(t)\ )$ from $(1{,}0)$
- $(A_B(t), B_B(t)\ )$ from $(0{,}1)$

Remarkably, $\frac{B_A(t)}{A_B(t)} = \frac{k_1}{k_{-1}} = K_{eq}$ is constant!

$$\mathcal{L}B_A(s) = \frac{k_1}{s^2 + (k_1 + k_{-1})s} \qquad \mathcal{L}A_B(s) = \frac{k_{-1}}{s^2 + (k_1 + k_{-1})s}$$

Yablonsky, G.S., Constales, D., Marin, G.B. Equilibrium relationships for non-equilibrium chemical dependencies. Chem. Eng. Sci. 66 (1) 111-114 (2011).

# Laplace domain solution

$$\begin{pmatrix}\mathcal{L}C_A(s)\\ \mathcal{L}C_B(s)\\ \mathcal{L}C_C(s)\end{pmatrix} = \frac{1}{s(s^2+(k_1^{+}+k_1^{-}+k_2^{+})s+k_1^{+}k_2^{+})} \times$$

$$\begin{pmatrix} s(s+k_1^{-}+k_2^{+}) & k_1^{-}s & 0\\ k_1^{+}s & s(k_1^{+}+s) & 0\\ k_1^{+}k_2^{+} & k_2^{+}(s+k_1^{+}) & s^2+(k_1^{+}+k_1^{-}+k_2^{+})s+k_1^{+}k_2^{+}\end{pmatrix}$$

$$\begin{pmatrix}C_A(0)\\ C_B(0)\\ C_C(0)\end{pmatrix}$$

The ratio of B from A to A from B is a constant, in fact the equilibrium constant of the first reaction step:

$$K_{eq} = \frac{k_1^{+}}{k_1^{-}} = \frac{C_{B_A}(t)}{C_{A_B}(t)}$$

# Reversible consecutive reactions

Next case: batch reactor, $A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B \overset{k_2}{\rightarrow} C$

- $\left(A_A(t), B_A(t), C_A(t)\right)$ from (1,0,0)
- $\left(A_B(t), B_B(t), C_B(t)\right)$ from (0,1,0)

$$t_{B_A \max} \equiv t_{A_B \max}?$$

Actually, $\dfrac{B_A(t)}{A_B(t)} = \dfrac{k_1}{k_{-1}} = K_{eq}$ is constant!

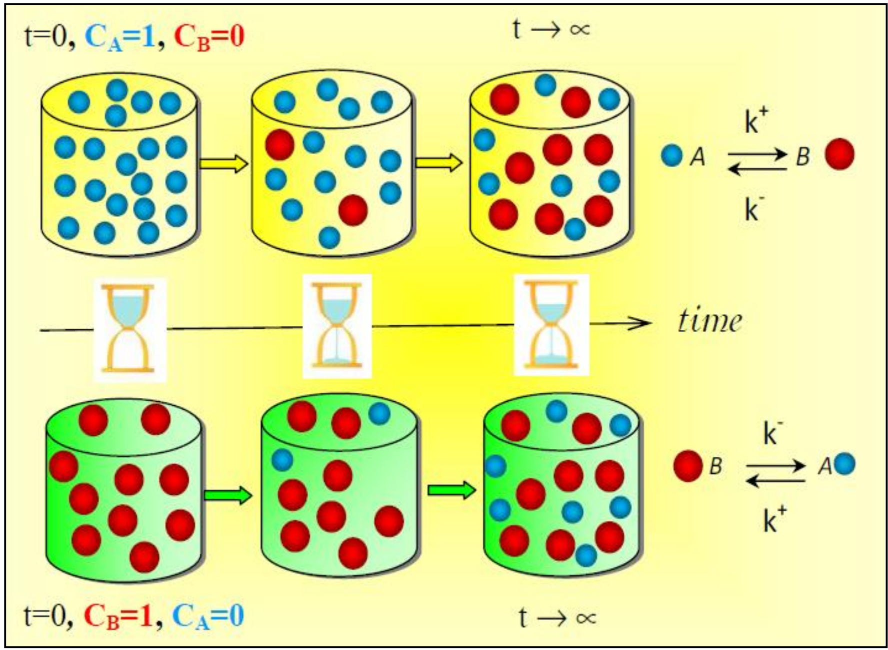
$$\mathcal{L}B_A(s) = \frac{k_1}{s^2 + (k_1 + k_{-1} + k_2)s + k_1 k_2} \quad \mathcal{L}A_B(s) = \frac{k_{-1}}{s^2 + (k_1 + k_{-1} + k_2)s + k_1 k_2}$$

Yablonsky, G.S., Constales, D., Marin, G.B. Equilibrium relationships for non-equilibrium chemical dependencies. Chem. Eng. Sci. 66 (1) 111-114 (2011).

# $A \leftrightarrows B \rightarrow C$ : dual experiments

We explore the behavior of $C_A(t)$, $C_B(t)$, and $C_C(t)$ relative to each other from two symmetrical initial conditions:

1) $C_{A,0} = 1$, $C_{B,0} = 0$;   and
2) $C_{A,0} = 0$, $C_{B,0} = 1$.



# Rigorous proof

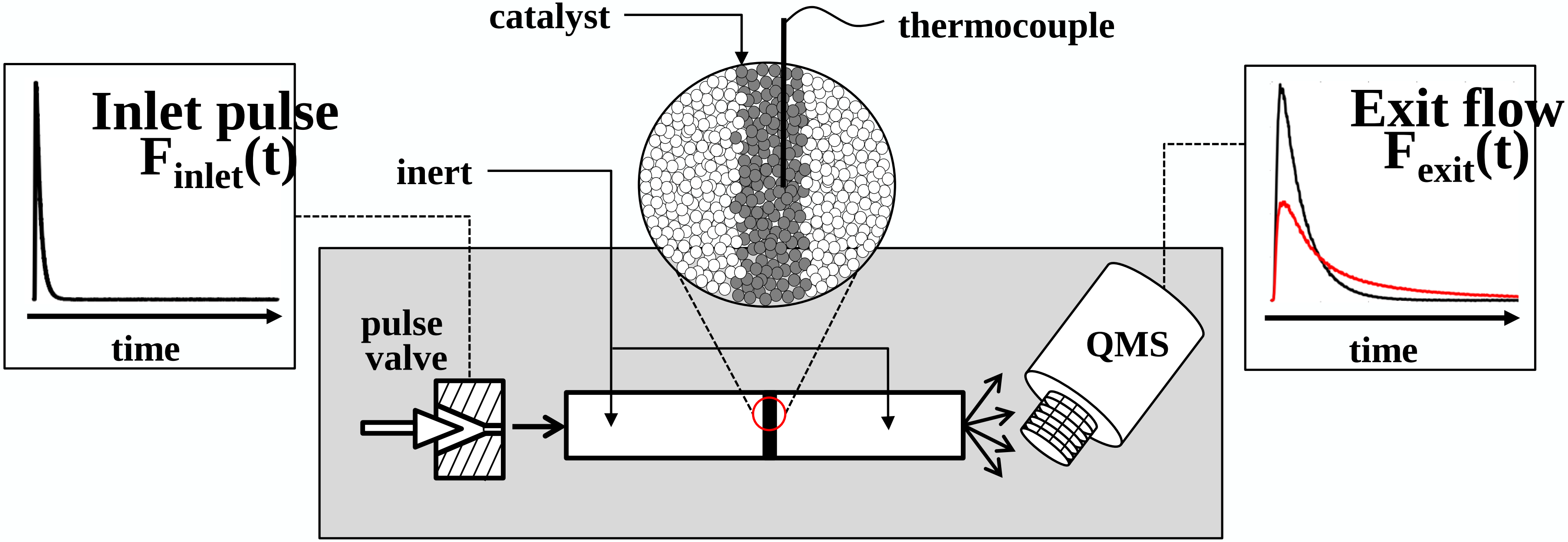
- For linear or linearized kinetics with microreversibility, $dx/dt = Kx$, the kinetic opretor K is symmetric in the entropic product. This form of Onsager reciprocal relations implies that that the shift in time, exp (Kt), is also a symmetric operator. This generates the reciprocity relations between the kinetic curves.
- *Yablonsky, Gorban, Constales, Galvita, Marin,” Reciprocal relations between kinetic curves”, EPL, 93(2011), 20004*

- This time invariance is a special case of a general result (Onsager reciprocity) for linear systems and some non-linear systems

# General time-invariances

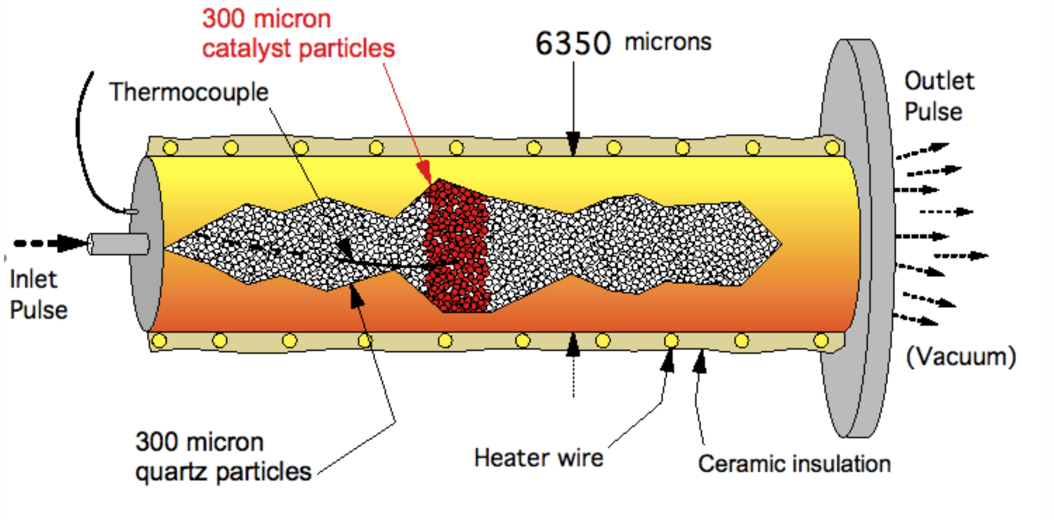
- We have also extended it to the TAP (Temporal Analysis of Products) reactor.

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

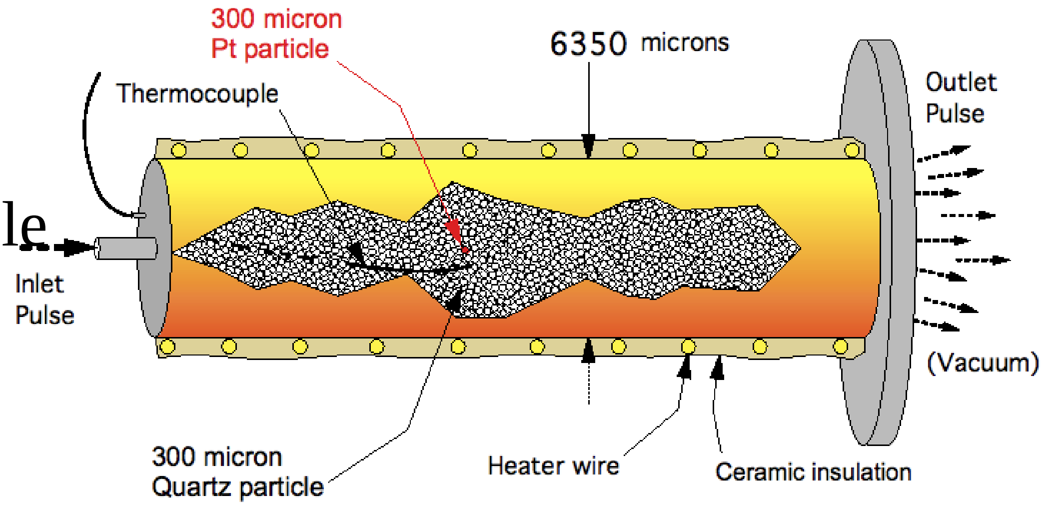


# Thin-zone and Single Particle Reactor Configurations

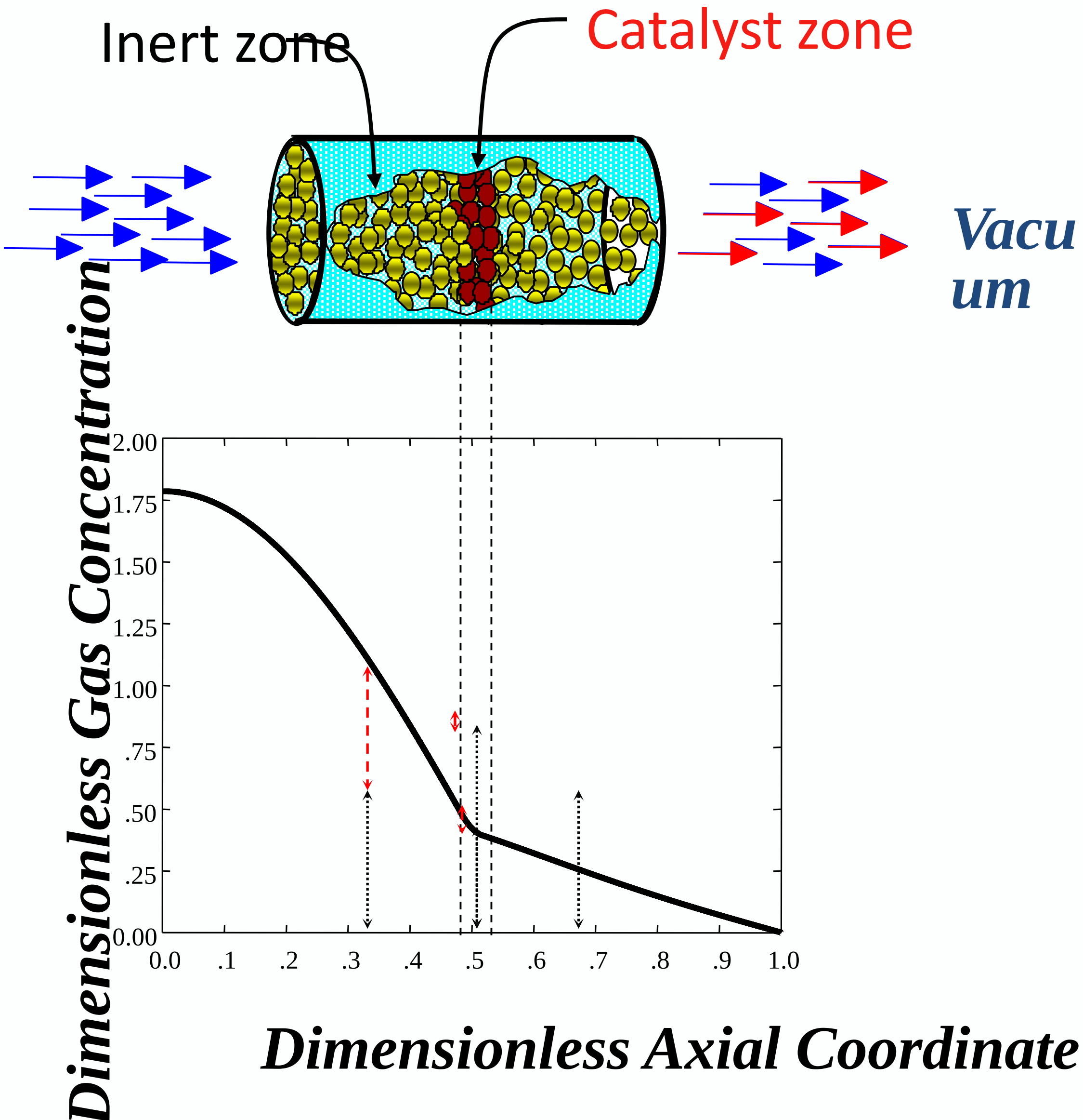
Thin-zone



Single-particle



# Thin-Zone TAP -Reactor (TZTR) Idea



- It was experimentally proven in TAP-studies of the Water-Gas- Shift reaction

# General time-invariances

TAP- experiments. Water-Gas-Shift

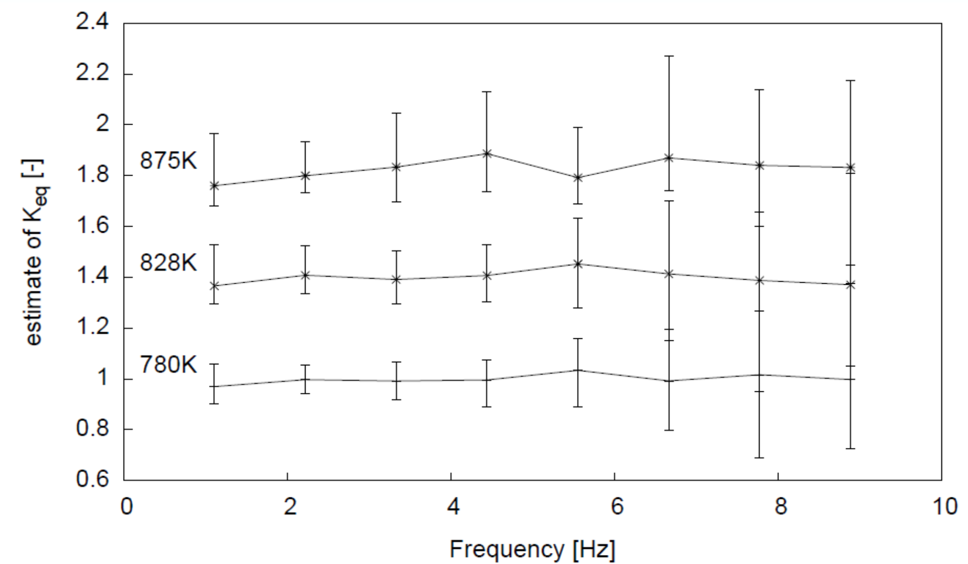
Two experiments:

1. $CO_2$ is pulsed. CO(t) is measured
2. CO is pulsed. $CO_2$ (t) is measured

Ratio $CO_2(t)$ / CO (t) = const

# General time-invariances

- We have also extended it to the TAP (Temporal Analysis of Products) reactor.



## Experimental Verification of Onsager Reciprocal Relations in Chemistry

The reciprocal relations were tested experimentally for many systems. In 1960, D. G. Miller wrote a remarkable review on experimental verification of the Onsager reciprocal relations which is often referred to even now. Analyzing many different cases of irreversible phenomena (thermoelectricity, electrokinetics, isothermal diffusion, etc), Miller found that these reciprocal relations are valid. However, regarding the chemical reactions, Miller’s point was : “The experimental studies of this phenomenon ...have been inconclusive, and the question is still open from an experimental point”

( Miller D. G., Chem. Rev., 60 (1960) 15.)

- A New Understanding:

Knowing the equilibrium composition (or equilibrium constants) and kinetic dependences experimentally measured from some initial conditions, one can determine kinetic dependences from other initial conditions.

# Questions

- (1) How many kinetic dependences do we have to determine in addition to knowing the equilibrium constants for this purpose?
- (3) What is the procedure for determining the unknown kinetic dependences
- based on the known ones
- (3) Are all these procedures successful or not?

Answer:

For n-linear chemical system, in addition to the equilibrium composition we have to know N x (N-1) /2 kinetic dependences.

E.g., for the classical 3-step Wei-Prater isomerization mechanism, we have to know

(3 x 2) / 2 = 3 kinetic dependences

# General Dogma

*A reminder on the general dogma*

**It is impossible to predict the temporal evolution of a reacting chemical system based on its description under equilibrium conditions**

# *Revisiting the dogma*

## NEW UNDERSTANDING

In some cases, knowing the thermodynamic characteristics and kinetic dependencies which start from some initial conditions, it is possible to predict kinetic behavior from other initial conditions.

- Goal: develop dual kinetic experiments for invariant quantities in electrochemical reactions:
  DUAL KINETIC
  CHRONOAMPEROMETRY

  (Kiss, 2014-2015)

# Dual Kinetic Chronoamperometry

## Consider first order reversible electrochemical reaction on a rotating disk electrode [7]

$$A^{+} + e^{-} \rightleftharpoons B$$

$a$: Nernst diffusion layer thickness
$c_A$ and $c_B$: near surface concentrations of $A$ and $B$
$c_A^0$ and $c_B^0$: bulk concentration of $A$ and $B$
$k_f(V)$ and $k_r(V)$: potential ($V$) dependent forward and reverse first-order rate constant
$D_A$, $D_B$: diffusion constants of A and B.
$k_f^0$ and $k_r^0$: rate constants at $V$=0
β: transfer coefficient
$R$: gas constant, $T$: temperature
Q: reaction quotient

$$\frac{\mathrm{d}c_A}{\mathrm{d}t} = \frac{2}{a}\left(-k_f(V)c_A + k_r(V)c_B\right) + \frac{2D_A}{a^2}\left(c_A^0 - c_A\right)$$

$$\frac{\mathrm{d}c_B}{\mathrm{d}t} = \frac{2}{a}\left(k_f(V)c_A - k_r(V)c_B\right) + \frac{2D_B}{a^2}\left(c_B^0 - c_B\right) \qquad (2)$$

$$k_f(V) = k_f^0 \exp\left[-(1-b)\frac{zF}{RT}V\right]$$

$$k_r(V) = k_r^0 \exp\left[b\frac{zF}{RT}V\right]$$

Thermodynamic equilibrium (Nernst potential):

$$E = E_0 - \frac{RT}{zF}\ln Q = E_0 - \frac{RT}{zF}\ln\frac{c_B^0}{c_A^0}$$

Current

$$i(t) = zF\left[-k_f(V)c_A(t) + k_r(V)c_B(t)\right]$$

# Methodology

- Thermodynamic equilibrium: The electrode potential is set to *V*=*E* and

$$\lim_{t\to\infty} i(t) = 0,\ \lim_{t\to\infty} c_A(t) = c_A^0,\ \lim_{t\to\infty} c_B(t) = c_B^0$$

- We shall seek invariant quantities in the ‘relaxation’ process to this equilibrium state defined by reaction quotient at the equilibrium state $Q = c_B^0/c_A^0$
- The experiments shall involve initial conditions with only one species present. To achieve this, we use pre-polarization experiment:
  - *‘Scenario 1’*: the electrode potential is set to large negative value in the mass-transfer limited region where all *A* is reduced to *B*, therefore, $c_A(t=0)=0$, $c_B(t=0)=c_B^0+c_A^0$
  - *‘Scenario 2’*: the electrode potential is set to large positive value in the mass-transfer limited region where all *B* is oxidized to *A*, therefore, $c_B(t=0)=0$, $c_A(t=0)=c_B^0+c_A^0$
- We shall measure the concentration of A in ‘Scenario 1’ and the concentration of B in ‘Scenario 2’.
- ***Hypothesis*: for simple electrochemical reaction studied here, the ratio of near surface concentrations $c_B/c_A$ at any time *t* will be an invariant quantity determined by the bulk concentrations $c_B^0/c_A^0$**

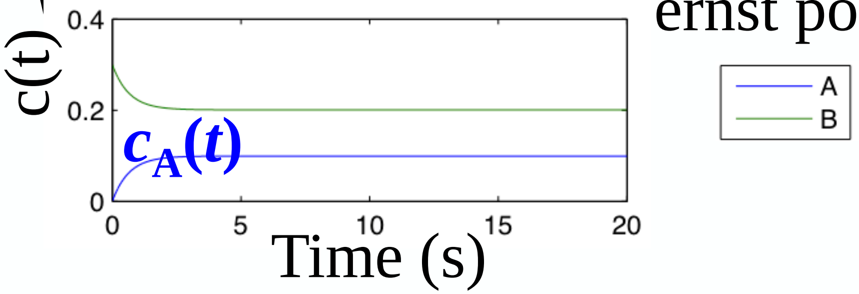
# Dual Kinetic Chronoamperometry
# Model simulations

- Equations 2 were numerically integrated.
- $c_A^0$ =0.1 M, $c_B^0$=0.2 M, Q=2
  $a$=0.01 cm, $z$=1, $T$=298 K, $D_A$ =$D_B$=$10^{-5}$ cm$^2$/s, β=0.5
  $k_f^0$ = 0.01 cm/s, and $k_r^0$=0.001 cm/s
- With these parameters the equilibrium:
  $V$=$E$=0.041 V, $c_A$ =0.1 M, $c_B$=0.2 M

‘Scenario 1’

$V$=-0.5 V for $t$< 0 s : cathodic limit

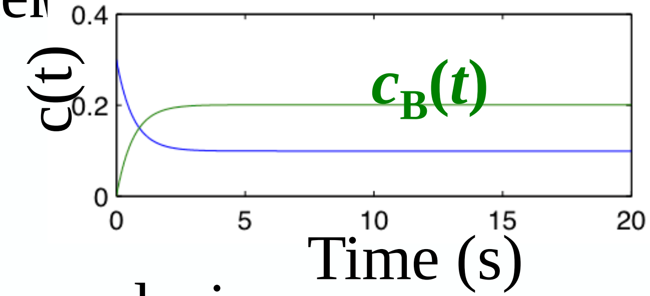
$V$=0.041 V for $t$> 0 s : Nernst potential



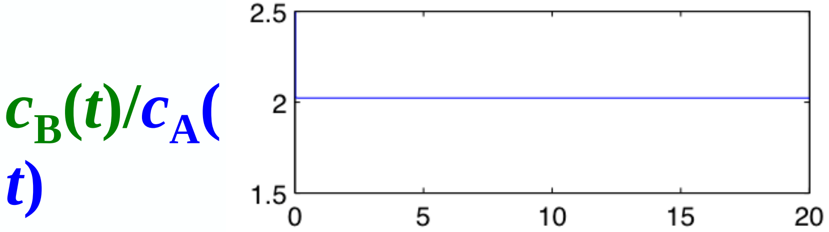
‘Scenario 2’

$V$=0.5 V for $t$< 0 s : anodic limit

$V$=0.041 V for $t$> 0 s : Nernst pote



Dual kinetic analysis



**The ratio of concentrations from dual kinetic experiments with symmetrical initial conditions is invariant quantity = Q: hypothesis is confirmed**

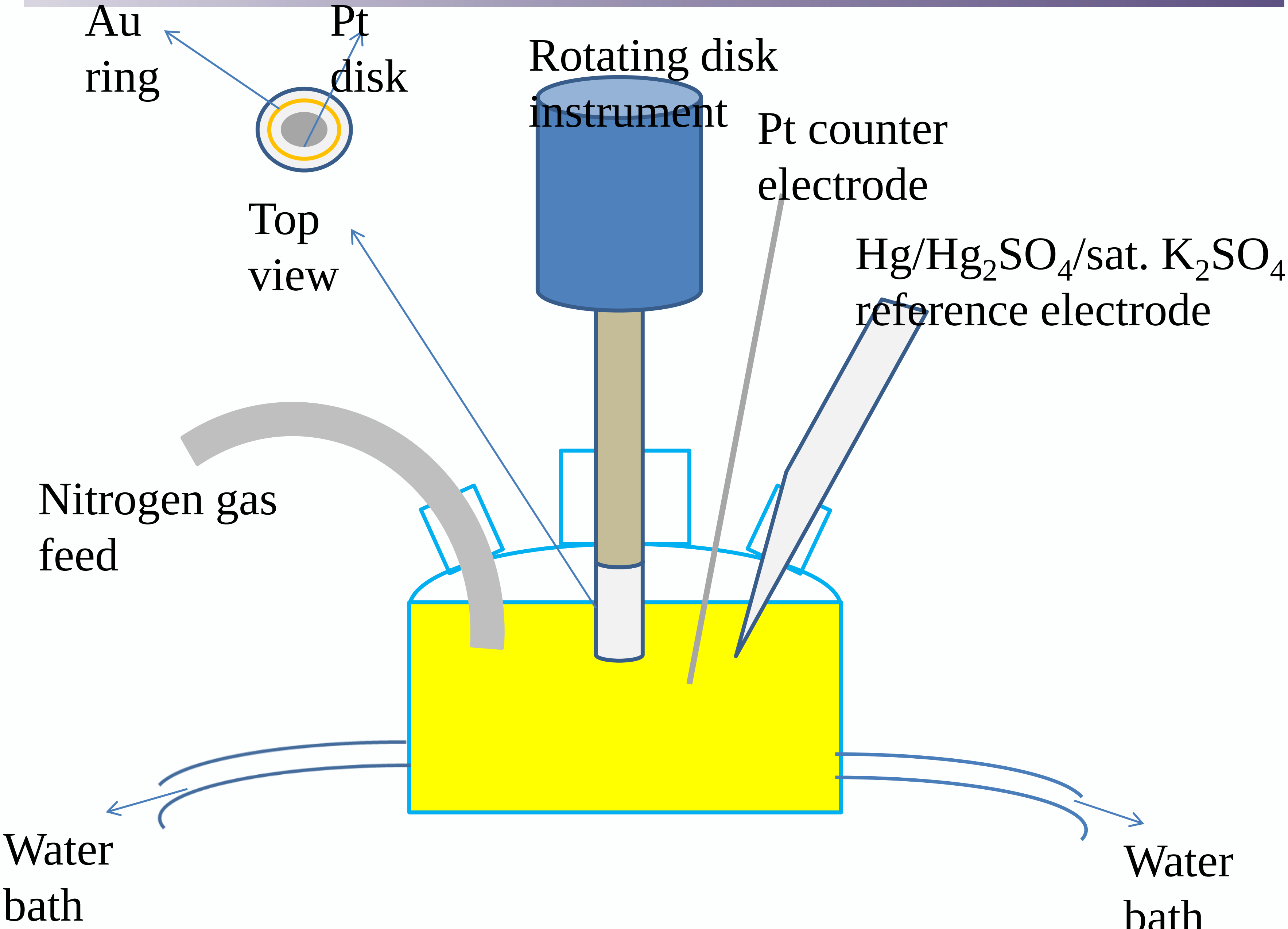
# Dual Kinetic Chronoamperometry Experiments

- Using ferrocyanide/ferricyanide system (A: ferricyanide, B: ferrocyanide)

$$\mathrm{Fe(CN)_6^{3-}} + e^- \leftrightharpoons \mathrm{Fe(CN)_6^{4-}}$$

- Applied potential is used to control the state of the system
  - Potential for the equilibrium state is open circuit potential (current =0) given by the Nernst equation based on the initial concentrations of the species
  - The symmetrical initial conditions were obtained with pre-polarization at the mass transfer limited regions in the anodic and cathodic direction.
  - The concentrations of ferrocyanide and ferricyanide were determined by shielding experiments with a ring electrode: ring-disk experiments
    Disk: reaction takes place
    Ring: measures concentrations

# Equipment



Au ring

Pt disk

Top view

Rotating disk instrument

Pt counter electrode

$Hg/Hg_2SO_4$/sat. $K_2SO_4$ reference electrode

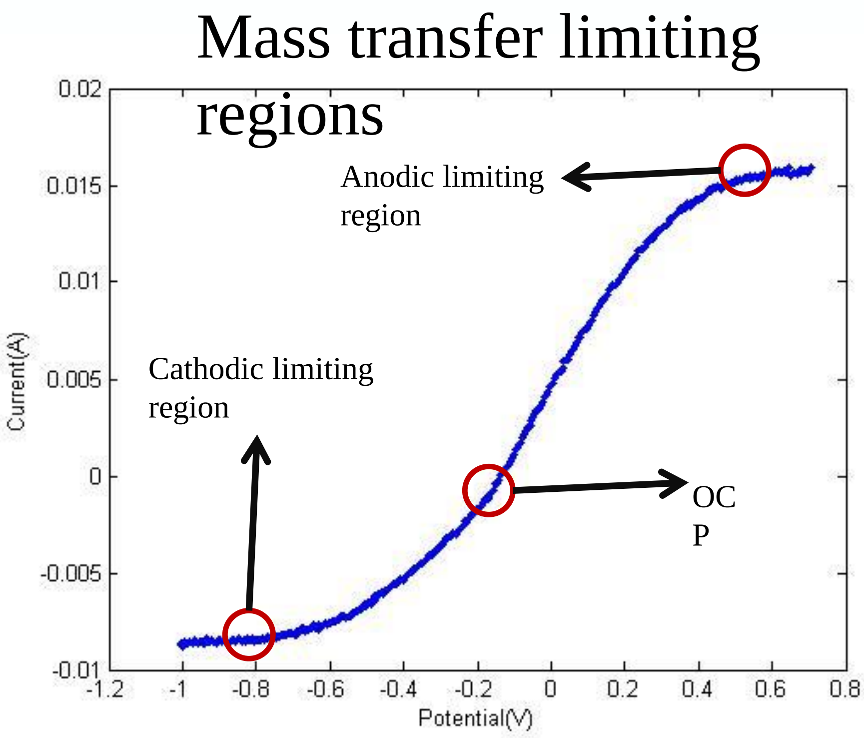
Nitrogen gas feed

Water bath

Water bath

# Equilibrium and limiting potentials

- Equilibrium potential (OCP) at current = 0
- Limiting potentials were found by linear sweep voltametry (LSV)
    - Start from equilibrium potential (open circuit potential, OCP) and scan potential until current no longer increases
    - Scan in both anodic and cathodic directions



Mass transfer limiting regions

Anodic limiting region

Cathodic limiting region

OCP

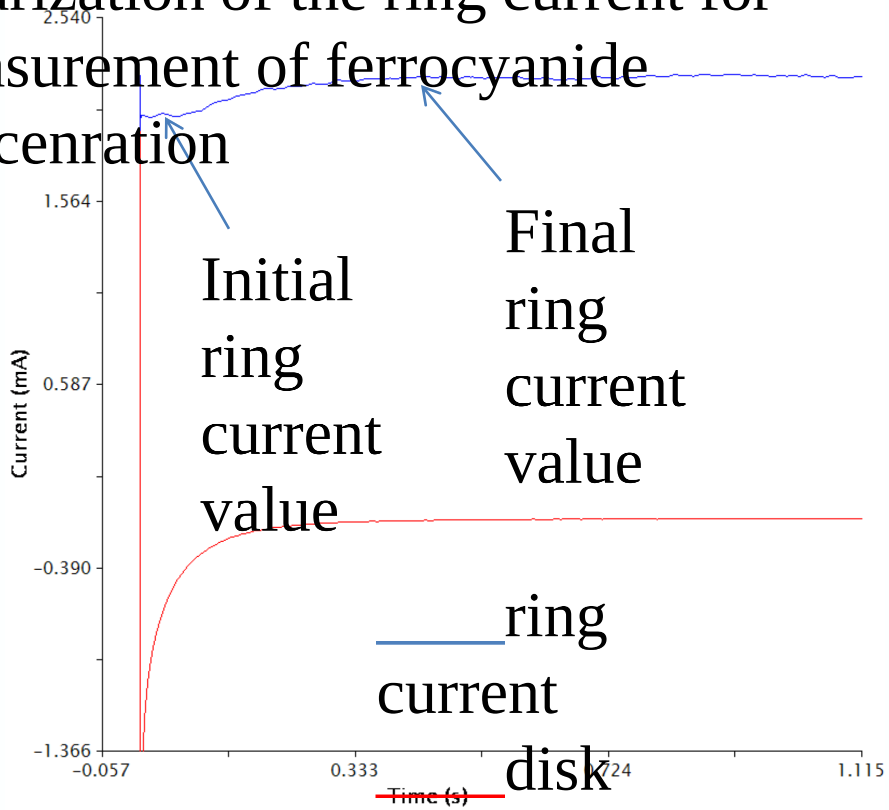
# Calculating concentration from ring current

- Shielding experiments: the change in ring current is proportional to concentration [7]
- For ferrocyanide: the ring is set to anodic potential of $V$=0.5 V.
  - When disk is at OCP, there is no shielding, therefore, the ring current $i_{r,1}$ corresponds to a near surface concentration that equals the bulk concentration:[$c_B^0$, $i_{r,1}$]
  - When disk is at anodic overpotential at mass transfer limit: all ferrocyanide is oxidized, the ring current $i_{r,2}$ is fully shielded, therefore, the near surface concentration is zero [0, $i_{r,2}$]
  - We used linear interpolation from above data for calculation of concentrations from the ring currents during the chronoamperometric experiment on the disk
- For ferrycianide concentration analogous technique was used but with cathodic potential of $V$=-0.8 V.

# Chronoamperometry

- During experiment disk and ring currents are measured at a data acquisition rate of 1 kHz.
- Dual kinetic measurement:
- ‘Scenario 1’:
  The disk current was cathodically pre-polarized at *V*=-0.8 V. At *t*=0 the disk potential was quickly switched to OCP. For ferro/ferricyanide concentration the ring is polarized anodically (*V*=0.5 V)/cathodically (*V*=-0.8 V) for the entire experiment.
- ‘Scenario 2’:
  The disk current was anodically pre-polarized at *V*=0.5 V. At *t*=0 the disk potential was quickly switched to OCP. For ferro/ferricyanide concentration the ring is polarized anodically (*V*=0.5 V)/cathodically (*V*=-0.8 V) for the entire experiment.
- c(ferrocyanide)$^0$= 0.02 M
  c(ferricyanide)$^0$= 0.01 M

‘Scenario 2’, with anodic polarization of the ring current for measurement of ferrocyanide concenration



Initial ring current value

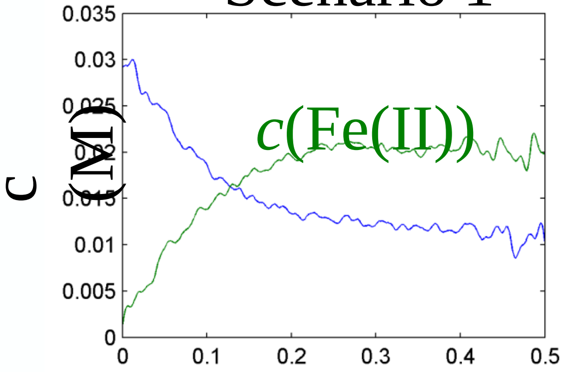
Final ring current value

ring current

disk current

# Concentrations: Experimental Results

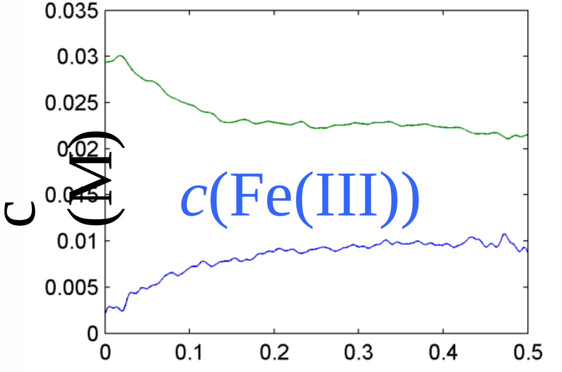
Scenario 1



Time (s)

___Fe(II)
___Fe(II)

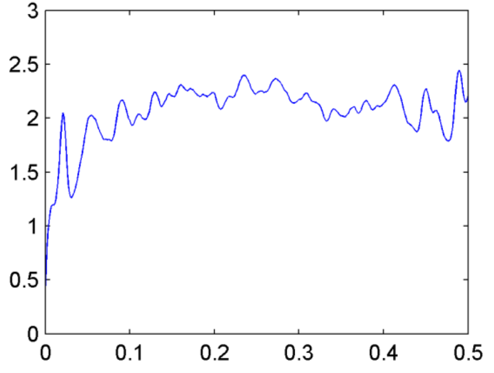
Scenario 2



Time (s)

Dual kinetic analysis

*c*(Fe(II)) /*c*(Fe(III))



Time (s)

**The ratio of concentrations from dual kinetic experiments with symmetrical initial conditions is approximately invariant quantity ≈ Q=2: hypothesis is experimentally confirmed**

# Conclusions

- Reciprocal relations between the kinetic curves provide a unique possibility to extract the non-steady state trajectory starting from one initial condition based only on the equilibrium constant and the trajectory which starts from the symmetrical initial condition.
- **Dual kinetic chronoamperometry** is proposed as a novel technique for exploration of kinetic features of electrochemical reactions
- Kinetic information is extracted from two experiments: each experiment consisted of setting the the disk electrode to an equivalent far-from-equilibrium potential, such as the anodic or cathodic limit, and allowing each to relax to equilibrium defined by the Nernst potential.
- Numerical simulations indicate that the proper ratio of the transient kinetic curves obtained from cathodic and anodic mass transfer limited regions give thermodynamic time invariances related to the reaction quotient of the bulk concentrations.
- Experimental tests with the ferrocyanide/ferricyanide system further confirm the principle: the concentrations of the oxidized and reduced species followed reciprocal paths as they relaxed toward equilibrium as long as both started from an equivalent state.
- Simplifying principles can exists in far-from-equilibrium chemical systems
- The results could impact (bio)fuel cell, sensor, and battery technology by predicting the concentrations and currents of the underlying non-steady state processes in a wide domain from thermodynamic principles and limited kinetic information.

# References

[1] N. G. van Kampen, Nonlinear irreversible processes, Physica **67** (1), 1–22 (1973).

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[5] G. S. Yablonsky, D. Constales, G. B. Marin, Chem. Eng. Sci. **66**, 111–114 (2011).

[6] D. Constales et al., Chem. Eng. Sci. **66**, 4683 (2011).

[7] A.J. Bard, L.R. Faulkner, Electrochemical Methods, Wiley, New York, 1980.

# II. EVENTS
# INTERSECTIONS
# COINCIDENCES

- Concepts of Events
  What are Events?
  Extrema, Intersections, Coincidences, Turning Points etc…
  Map of Events.
  Concepts of Ensemble of Experiments: Experiments with different Initial conditions

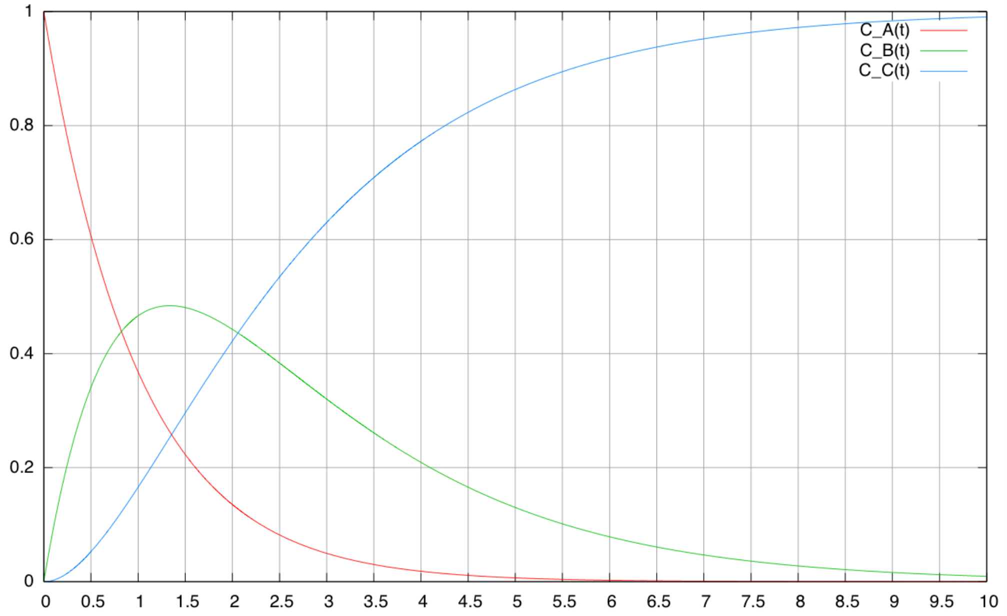
# A. Coincidences

- Surprising properties of the simple kinetic models; in particular, A->B->C.

$$\frac{dC_A}{dt} = -k_1 C_A,$$

$$\frac{dC_B}{dt} = k_1 C_A - k_2 C_B,$$

$$\frac{dC_C}{dt} = k_2 C_B,$$



# Solutions (known before)

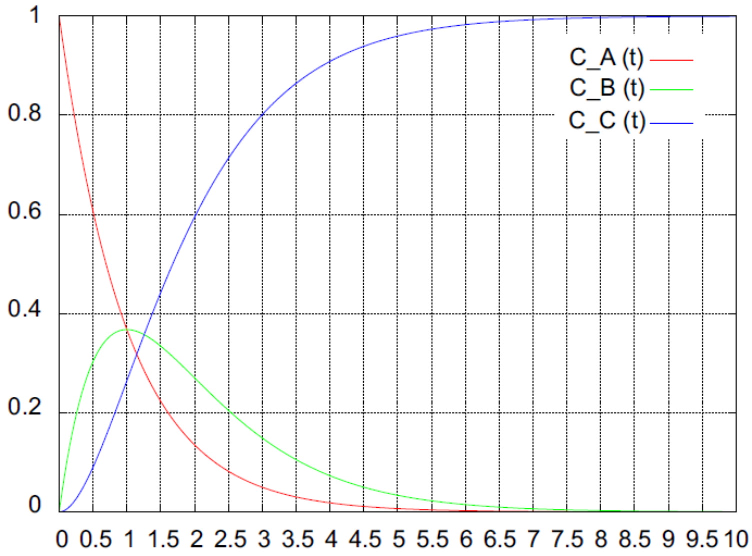
$$C_A(t) = C_{A,0}\exp(-k_1 t),$$

$$\begin{aligned} C_B(t) = {} & C_{A,0} k_1 \frac{\exp(-k_1 t) - \exp(-k_2 t)}{k_2 - k_1} \\ & + C_{B,0}\exp(-k_2 t), \end{aligned}$$

$$\begin{aligned} C_C(t) = {} & C_{A,0}\left[1 - \frac{k_2\exp(-k_1 t) - k_1\exp(-k_2 t)}{k_2 - k_1}\right] \\ & + C_{B,0}(1 - \exp(-k_2 t)) \end{aligned}$$

# Intersections

Depending on the parameter values and initial conditions, transient concentration curves of species A and B may intersect once or not intersect at all. The concentration transients of species C always intersect the concentration transients of A and B.



# Coincidences (cont'd)

- A simple problem is posed: what do we know about the points of intersection, the maximum point of $C_B(t)$, and their ordering?

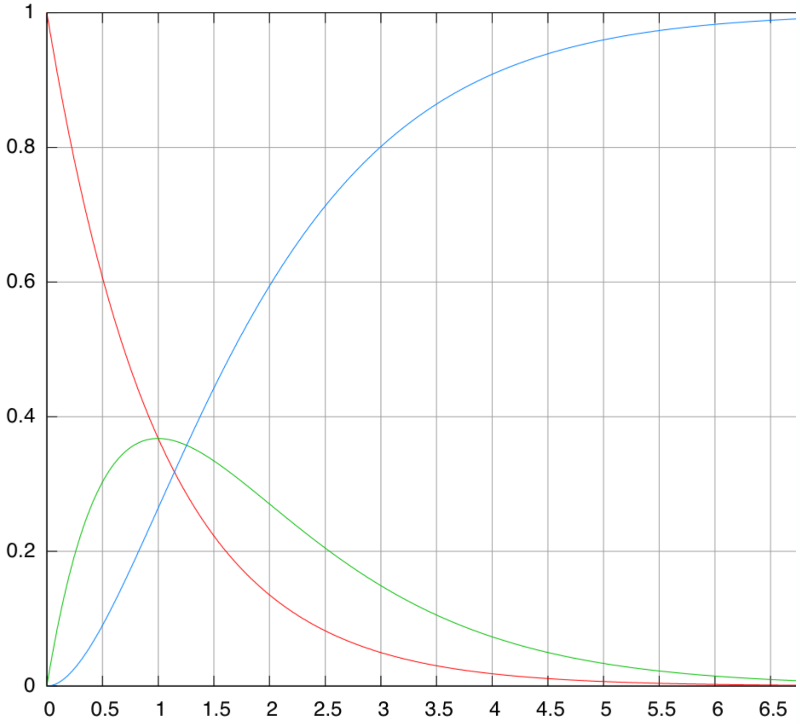
Example: $k_1 = k_2$

We call it Euler point.

$k_1 = k_2 = 1\ \mathrm{s}^{-1}$

$t_{B,max} = 1\ \mathrm{s}$

$C_{A,intersect} = C_{B,intersect} = 1/e$

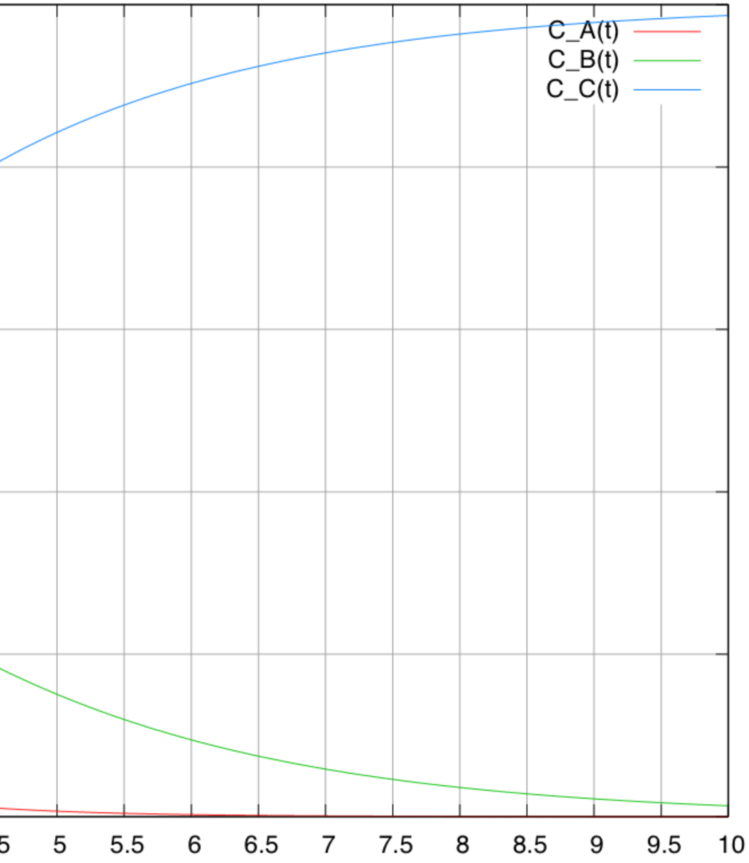


# Coincidences (cont'd)

- Nonlinear problem, even for a linear system.
- Many analytical results can be obtained.
- Of 612 possible arrangements, only six can actually occur.
- We introduce separation points for domains
- A(cme), G(olden), E(uler), L(ambert),O(sculation), T(riad) points.

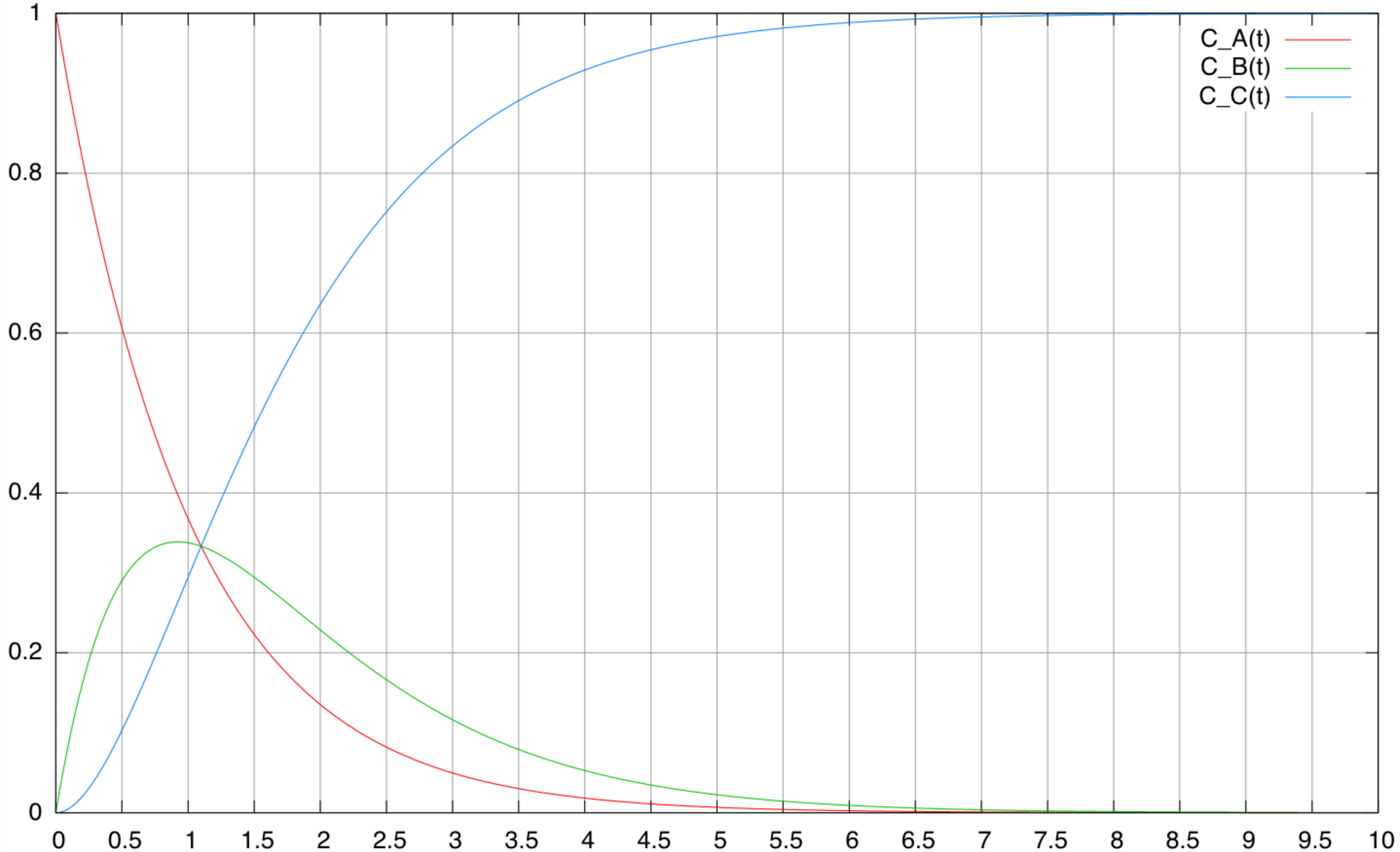
# Coincidences (cont’d)

- Acme, $k_2 = k_1/2$



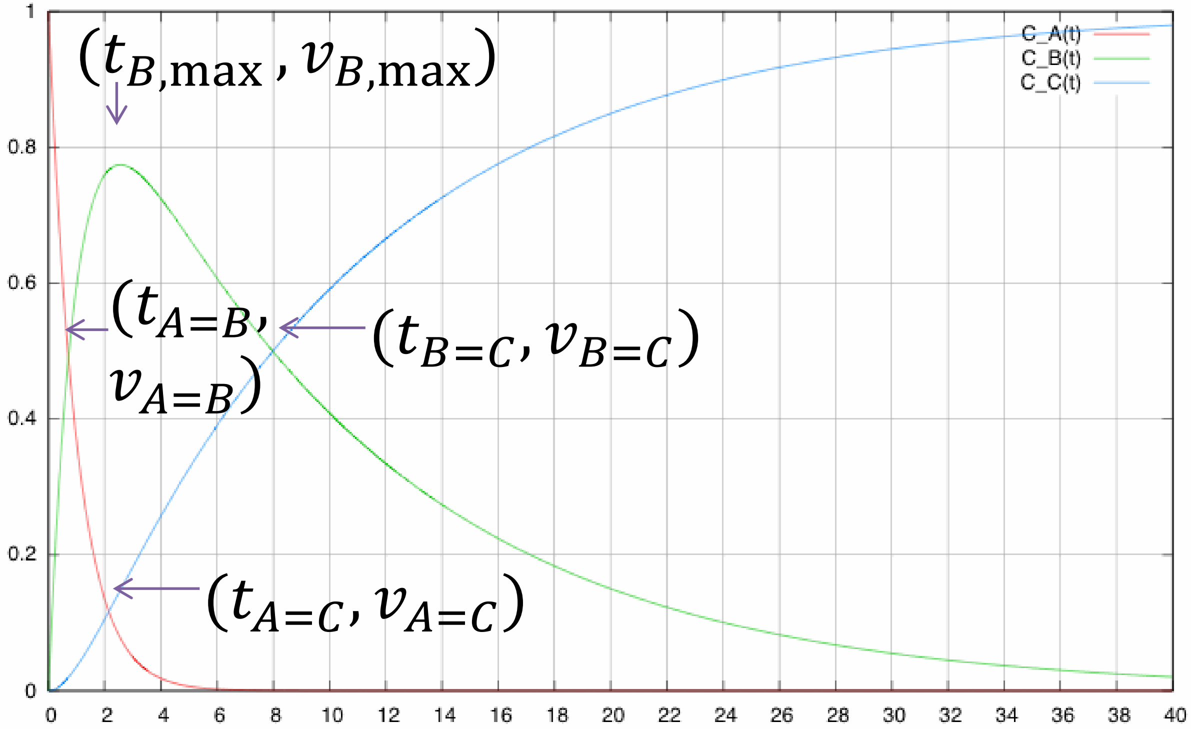
# Coincidences (cont'd)

- Lambert, $k_2 = 1.1739\ldots\ k_1$



# Consecutive reactions

## Linear kinetics in batch reactor, $A \xrightarrow{k_1} B \xrightarrow{k_2} C$



$t_{A=B} < t_{A=C} < t_{B,\max} < t_{B=C}$

$v_{A=C} < v_{A=B} < v_{B=C} < v_{B,\max}$

Yablonsky, G.S., Constales, D., Marin, G.B. Coincidences in chemical kinetics: Surprising news about simple reactions. Chem. Eng. Sci. 65 (23) 6065-6076 (2010).

# Coincidences (cont’d)

Inspecting the peculiarities of the experimental data, we may immediately infer the domain of the parameters.

Intersections, extrema and their ordering are an important source of as yet unexploited information.

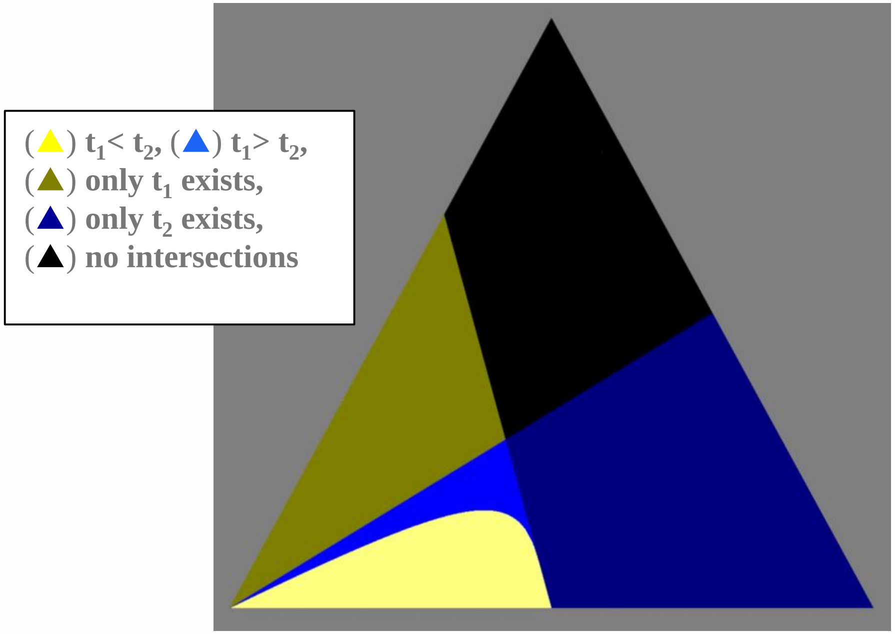
# Consecutive reactions with one reversible step

Batch reactor, $A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B \xrightarrow{k_2} C$

# Coincidences

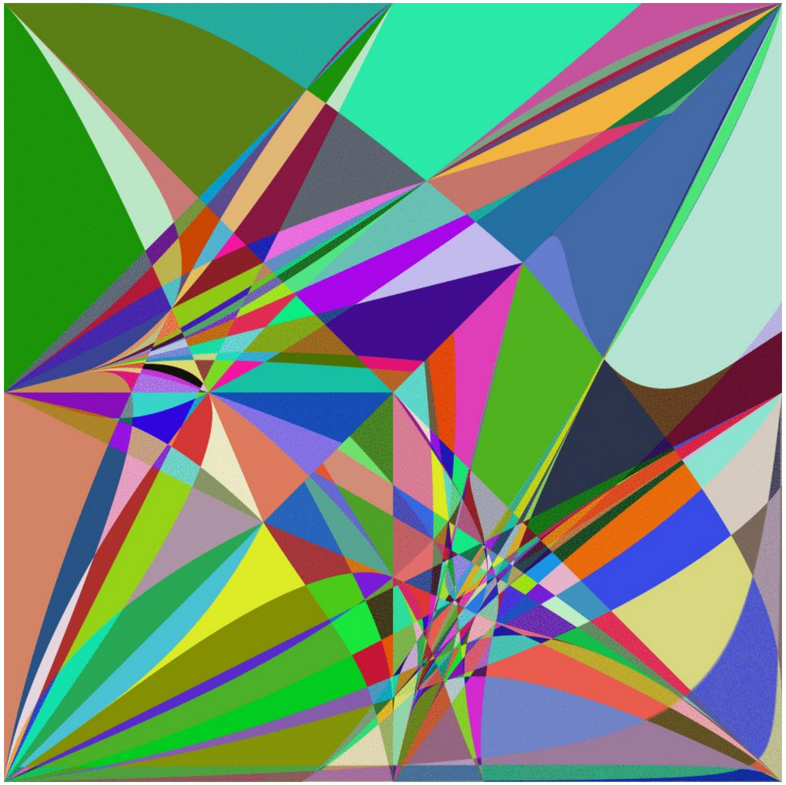
The intersections between concentration transients can be traced systematically and represented in parameter space: e.g. we show here the comparison between the intersection times of A from A with B from A ($t_1$) and that of A from B with B from B ($t_2$). The rate constants are used as barycentric coordinates.

The coincidence proper ($t_1=t_2$) occurs on the curved line separating the yellow and blue domains.



# Parametric subdomains

Combining all intersections in time and value an intricate map is obtained…
where each different patch is a qualitatively separate subdomain:
It is similar to abstract compositions
by Felix De Boeck (1898-1995):

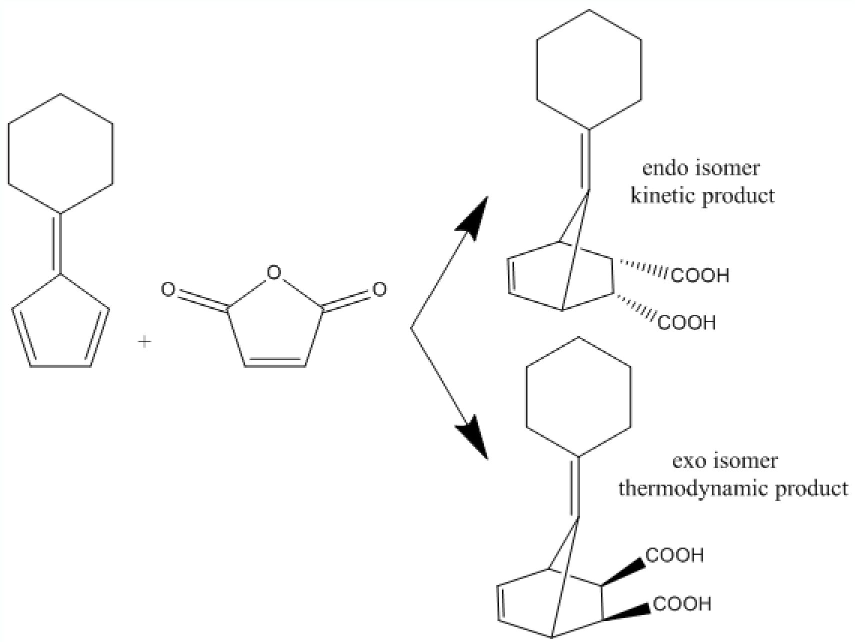


- **SIMPLE IS COMPLEX**

# III.

# Thermodynamic and Kinetic Control: Switching Point

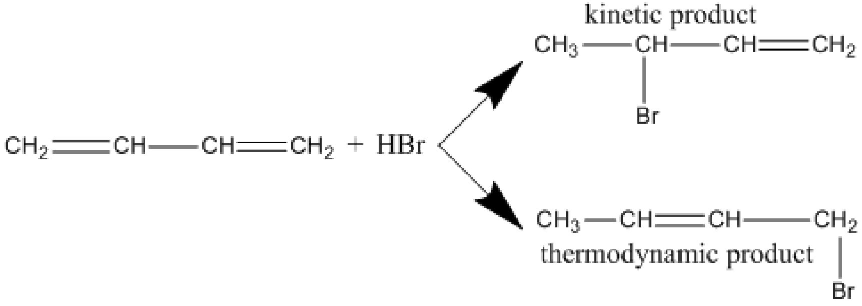
# kinetic vs thermodynamic control



* First mention in 1944, reaction of fulvene with maleic anhydride:

“*while the* endo *isomer is formed more rapidly, longer reaction times, as well as relatively elevated temperatures, result in higher* exo/endo *ratios. These facts must be considered in the light of the remarkable stability of the* exo-*compound on the one hand, and the very facile dissociation of the* endo *isomer on the other*”

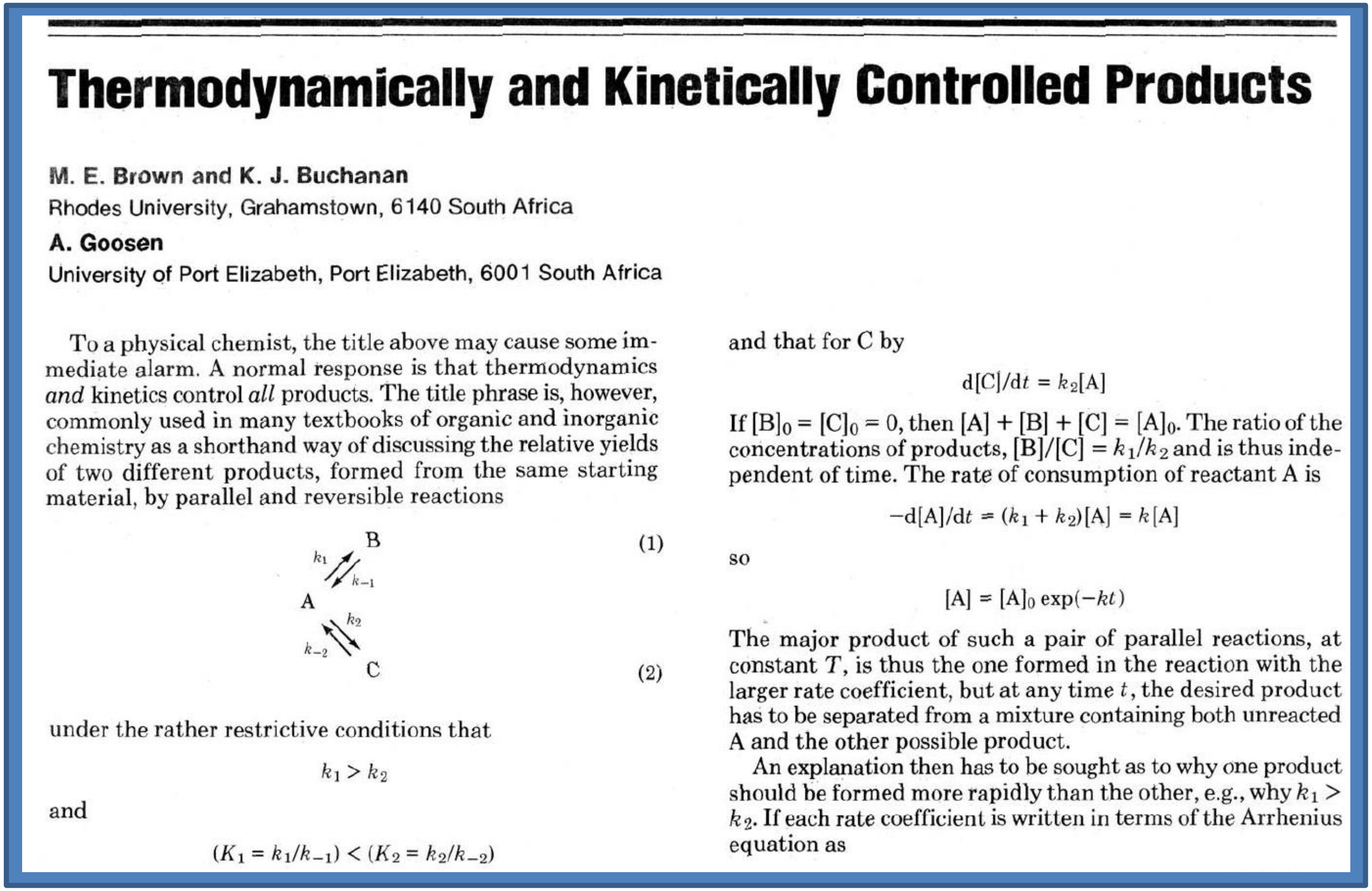
# kinetic vs thermodynamic control



Typical reaction in basic chemistry textbooks:

hydrohalogenation of 1,3-butadiene

# kinetic vs thermodynamic control



## Thermodynamically and Kinetically Controlled Products

**M. E. Brown and K. J. Buchanan**
Rhodes University, Grahamstown, 6140 South Africa
**A. Goosen**
University of Port Elizabeth, Port Elizabeth, 6001 South Africa

To a physical chemist, the title above may cause some immediate alarm. A normal response is that thermodynamics *and* kinetics control *all* products. The title phrase is, however, commonly used in many textbooks of organic and inorganic chemistry as a shorthand way of discussing the relative yields of two different products, formed from the same starting material, by parallel and reversible reactions

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \qquad (1)$$

$$A \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} C \qquad (2)$$

under the rather restrictive conditions that

$$k_1 > k_2$$

and

$$(K_1 = k_1/k_{-1}) < (K_2 = k_2/k_{-2})$$

and that for C by

$$d[C]/dt = k_2[A]$$

If $[B]_0 = [C]_0 = 0$, then $[A] + [B] + [C] = [A]_0$. The ratio of the concentrations of products, $[B]/[C] = k_1/k_2$ and is thus independent of time. The rate of consumption of reactant A is

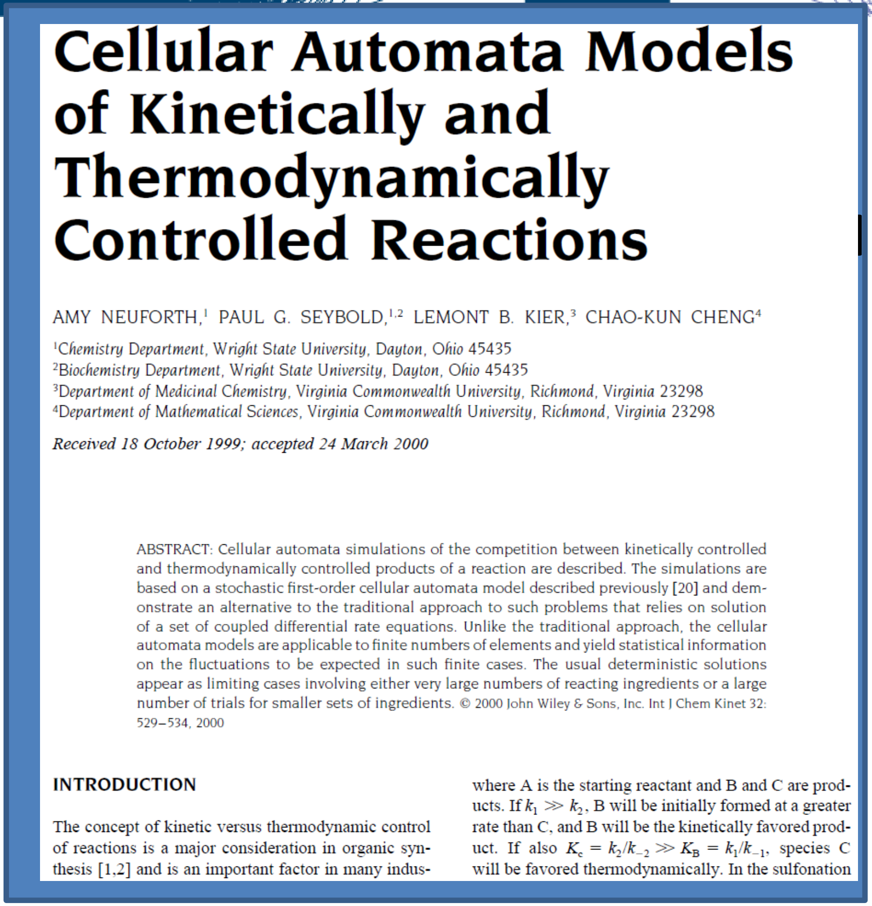
$$-d[A]/dt = (k_1 + k_2)[A] = k[A]$$

so

$$[A] = [A]_0 \exp(-kt)$$

The major product of such a pair of parallel reactions, at constant $T$, is thus the one formed in the reaction with the larger rate coefficient, but at any time $t$, the desired product has to be separated from a mixture containing both unreacted A and the other possible product.

An explanation then has to be sought as to why one product should be formed more rapidly than the other, e.g., why $k_1 > k_2$. If each rate coefficient is written in terms of the Arrhenius equation as



# Cellular Automata Models of Kinetically and Thermodynamically Controlled Reactions

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[3]*Department of Medicinal Chemistry, Virginia Commonwealth University, Richmond, Virginia 23298*
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*Received 18 October 1999; accepted 24 March 2000*

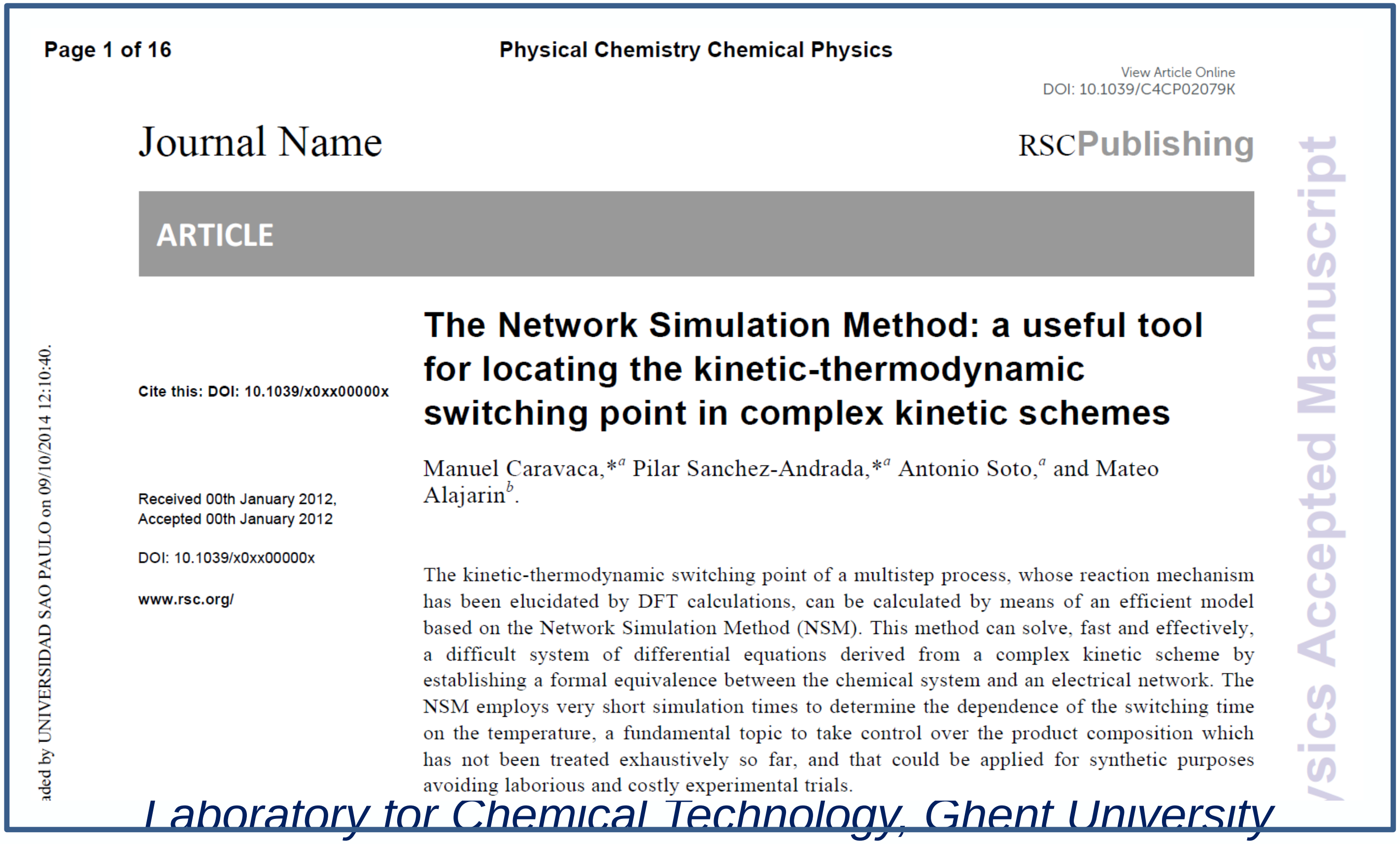
ABSTRACT: Cellular automata simulations of the competition between kinetically controlled and thermodynamically controlled products of a reaction are described. The simulations are based on a stochastic first-order cellular automata model described previously [20] and demonstrate an alternative to the traditional approach to such problems that relies on solution of a set of coupled differential rate equations. Unlike the traditional approach, the cellular automata models are applicable to finite numbers of elements and yield statistical information on the fluctuations to be expected in such finite cases. The usual deterministic solutions appear as limiting cases involving either very large numbers of reacting ingredients or a large number of trials for smaller sets of ingredients. © 2000 John Wiley & Sons, Inc. Int J Chem Kinet 32: 529–534, 2000

## INTRODUCTION

The concept of kinetic versus thermodynamic control of reactions is a major consideration in organic synthesis [1,2] and is an important factor in many indus-

where A is the starting reactant and B and C are products. If $k_1 \gg k_2$, B will be initially formed at a greater rate than C, and B will be the kinetically favored product. If also $K_c = k_2/k_{-2} \gg K_B = k_1/k_{-1}$, species C will be favored thermodynamically. In the sulfonation

# application



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ARTICLE

## The Network Simulation Method: a useful tool for locating the kinetic-thermodynamic switching point in complex kinetic schemes

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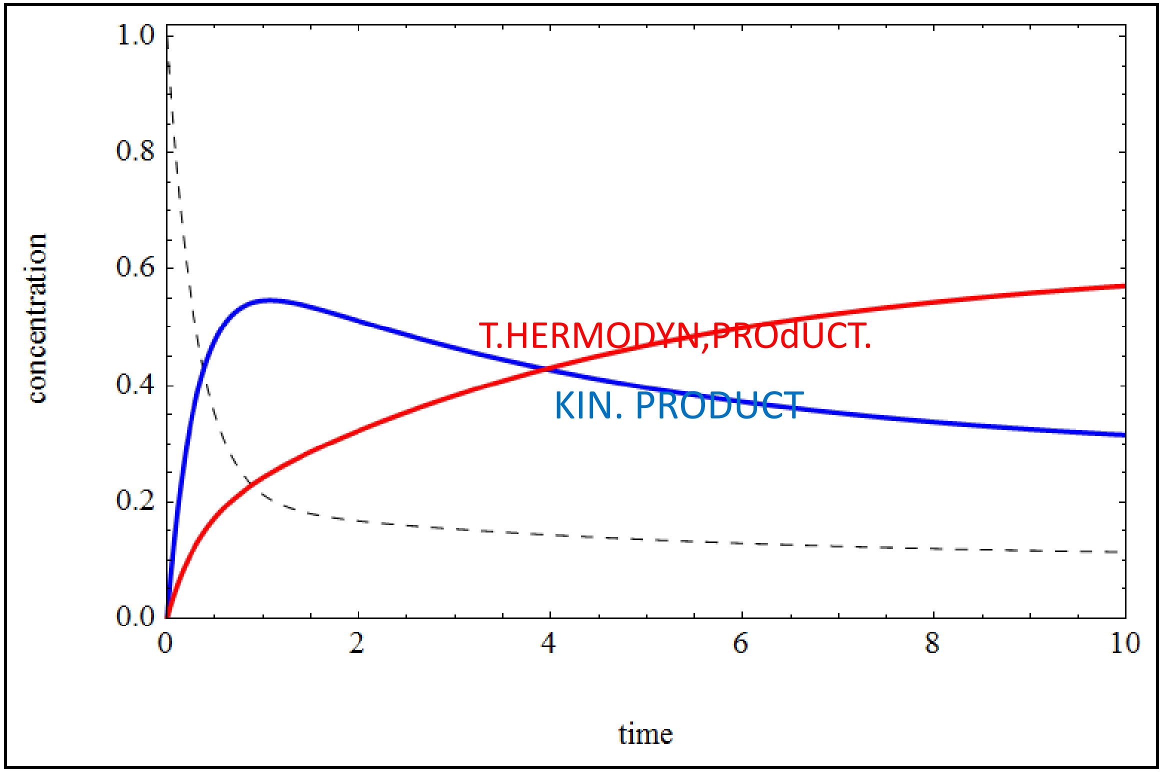
www.rsc.org/

Manuel Caravaca,*[a] Pilar Sanchez-Andrada,*[a] Antonio Soto,[a] and Mateo Alajarin[b].

The kinetic-thermodynamic switching point of a multistep process, whose reaction mechanism has been elucidated by DFT calculations, can be calculated by means of an efficient model based on the Network Simulation Method (NSM). This method can solve, fast and effectively, a difficult system of differential equations derived from a complex kinetic scheme by establishing a formal equivalence between the chemical system and an electrical network. The NSM employs very short simulation times to determine the dependence of the switching time on the temperature, a fundamental topic to take control over the product composition which has not been treated exhaustively so far, and that could be applied for synthetic purposes avoiding laborious and costly experimental trials.

From: Caravaca M., Sanchez-Andrada P., Soto A., Alajarin M., Phys. Chem. Chem. Phys., 16 (2014) 25409.



$$A \underset{k_3}{\overset{k_1}{\rightleftarrows}} K \qquad A \underset{k_4}{\overset{k_2}{\rightleftarrows}} T$$

crossing point
and
switching point

# kinetic vs thermodynamic control

mathematical resolution

$$A \underset{k_3}{\overset{k_1}{\rightleftarrows}} K \qquad A \underset{k_4}{\overset{k_2}{\rightleftarrows}} T$$

$$\begin{cases} \dfrac{\mathrm{dA(t)}}{\mathrm{dt}} = -(\mathrm{k_1} + \mathrm{k_2})\mathrm{A(t)} + \mathrm{k_3K(t)} + \mathrm{k_4T(t)} \\ \dfrac{\mathrm{dK(t)}}{\mathrm{dt}} = \mathrm{k_1A(t)} - \mathrm{k_3K(t)} \\ \dfrac{\mathrm{dT(t)}}{\mathrm{dt}} = \mathrm{k_2A(t)} - \mathrm{k_4T(t)} \end{cases}$$

# kinetic vs thermodynamic control

mathematical resolution

$$A \overset{k_1}{\underset{k_3}{\rightleftarrows}} K \qquad A \overset{k_2}{\underset{k_4}{\rightleftarrows}} T$$

$$\begin{cases} \dfrac{\mathrm{dA(t)}}{\mathrm{dt}} = -(\mathrm{k_1} + \mathrm{k_2})\mathrm{A(t)} + \mathrm{k_3 K(t)} + \mathrm{k_4 T(t)} \\ \dfrac{\mathrm{dK(t)}}{\mathrm{dt}} = \mathrm{k_1 A(t)} - \mathrm{k_3 K(t)} \\ \dfrac{\mathrm{dT(t)}}{\mathrm{dt}} = \mathrm{k_2 A(t)} - \mathrm{k_4 T(t)} \end{cases}$$

$$\mathrm{A(t)} = \mathrm{A_{eq}} + \left(\mathrm{A_o} - \mathrm{A_{eq}} - \mathrm{A_x}\right)\mathrm{e}^{-\lambda_\mathrm{p}\,\mathrm{t}} + \mathrm{A_x}\mathrm{e}^{-\lambda_\mathrm{m}\,\mathrm{t}}$$

# kinetic vs thermodynamic control

mathematical resolution

$$A \underset{k_3}{\overset{k_1}{\rightleftarrows}} K \qquad A \underset{k_4}{\overset{k_2}{\rightleftarrows}} T$$

$$\begin{cases} \dfrac{\mathrm{dA(t)}}{\mathrm{dt}} = -(\mathrm{k_1} + \mathrm{k_2})\mathrm{A(t)} + \mathrm{k_3 K(t)} + \mathrm{k_4 T(t)} \\ \dfrac{\mathrm{dK(t)}}{\mathrm{dt}} = \mathrm{k_1 A(t)} - \mathrm{k_3 K(t)} \\ \dfrac{\mathrm{dT(t)}}{\mathrm{dt}} = \mathrm{k_2 A(t)} - \mathrm{k_4 T(t)} \end{cases}$$

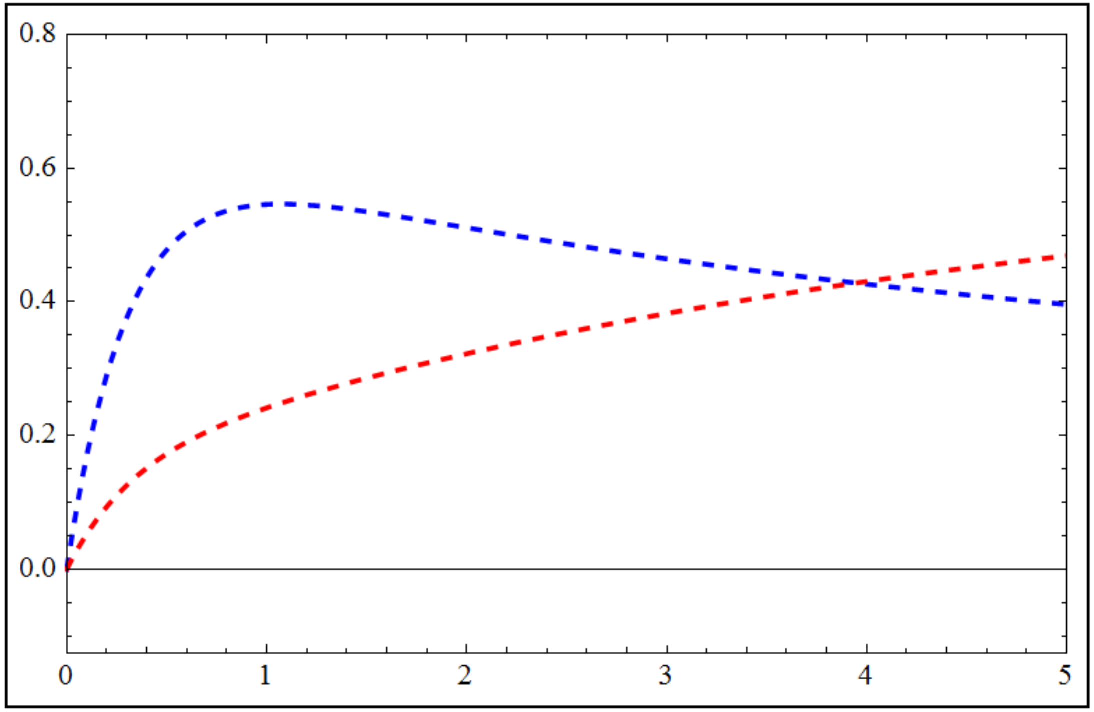
$$\mathrm{A(t)} = \mathrm{A_{eq}} + \left(\mathrm{A_o} - \mathrm{A_{eq}} - \mathrm{A_x}\right)\mathrm{e}^{-\lambda_\mathrm{p}\,\mathrm{t}} + \mathrm{A_x}\mathrm{e}^{-\lambda_\mathrm{m}\,\mathrm{t}}$$

# the switching point $t_s$

equality of rates of formation

$$\left.\frac{\mathrm{dK(t)}}{\mathrm{dt}}\right|_{\mathrm{t}} = \left.\frac{\mathrm{dT(t)}}{\mathrm{dt}}\right|$$

$A \underset{k_3}{\overset{k_1}{\rightleftarrows}} K \qquad A \underset{k_4}{\overset{k_2}{\rightleftarrows}} T$



K(t) ---

T(t) ---

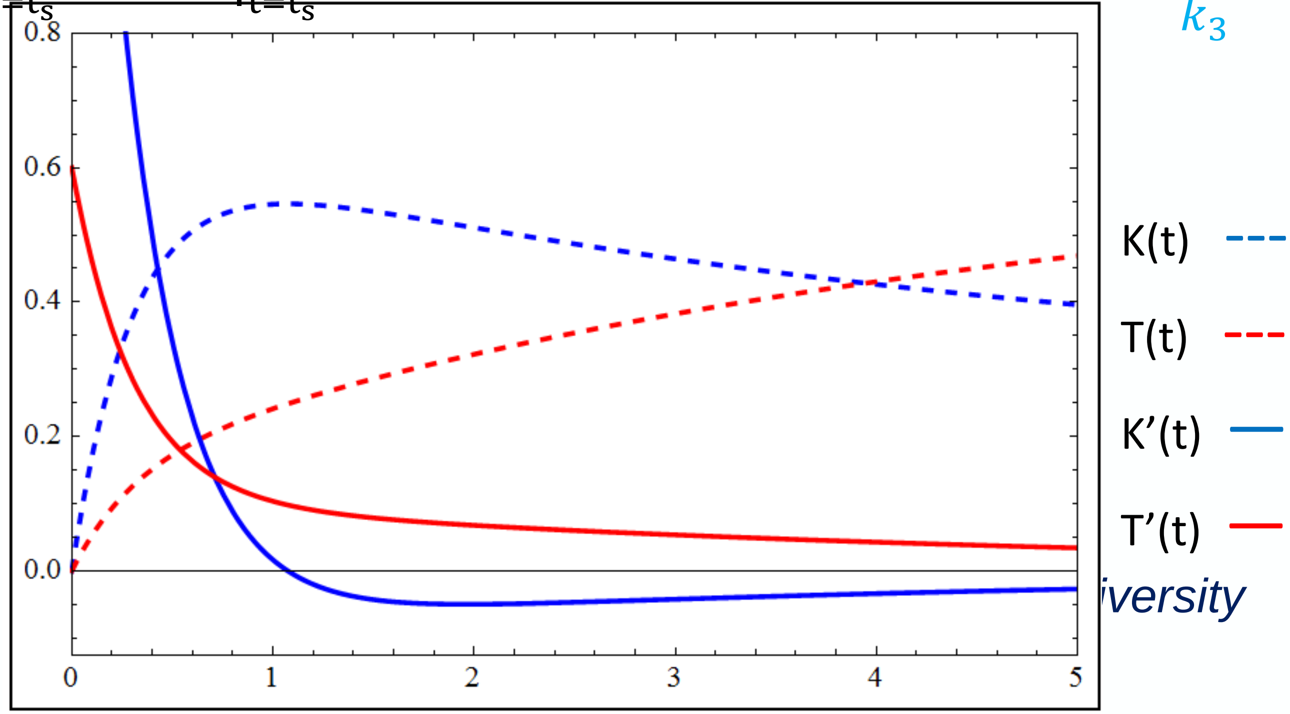
*iversity*

# the switching point $t_s$

equality of rates of formation

$$\left.\frac{dK(t)}{dt}\right|_{t=t_s} = \left.\frac{dT(t)}{dt}\right|_{t=t_s}$$

$$A \underset{k_3}{\overset{k_1}{\rightleftarrows}} K \qquad A \underset{k_4}{\overset{k_2}{\rightleftarrows}} T$$



# the switching point $t_s$

equality of rates of formation

$$\left.\frac{\mathrm{dK(t)}}{\mathrm{dt}}\right|_{\mathrm{t=t_s}} = \left.\frac{\mathrm{dT(t)}}{\mathrm{dt}}\right|_{\mathrm{t=t_s}}$$

$$\boxed{\mathrm{t_s} = \frac{\log\left(\frac{\lambda_\mathrm{p} - \Delta}{\lambda_\mathrm{m} - \Delta}\right)}{\lambda_\mathrm{p} - \lambda_\mathrm{m}}}$$

$$A \underset{k_3}{\overset{k_1}{\rightleftarrows}} K \qquad A \underset{k_4}{\overset{k_2}{\rightleftarrows}} T$$

# the switching point $t_s$

equality of rates of formation

$$\left.\frac{dK(t)}{dt}\right|_{t=t_s} = \left.\frac{dT(t)}{dt}\right|_{t=t_s}$$

$$A \underset{k_3}{\overset{k_1}{\rightleftarrows}} K \qquad A \underset{k_4}{\overset{k_2}{\rightleftarrows}} T$$

$$\boxed{t_s = \frac{\log\left(\frac{\lambda_p - \Delta}{\lambda_m - \Delta}\right)}{\lambda_p - \lambda_m}}$$

where

$$\Delta = \lambda_p \lambda_m \left(\frac{(K_{eq} - K_o) - (T_{eq} - T_o)}{(A_o k_1 - K_o k_3) - (A_o k_2 - T_o k_4)}\right)$$

# the switching point $t_s$

$$\left.\frac{dK(t)}{dt}\right|_{t=t_s} = \left.\frac{dT(t)}{dt}\right|_{t=t_s}$$

$$A \underset{k_3}{\overset{k_1}{\rightleftarrows}} K \qquad A \underset{k_4}{\overset{k_2}{\rightleftarrows}} T$$

$$\boxed{t_s = \frac{\log\left(\dfrac{\lambda_p - \Delta}{\lambda_m - \Delta}\right)}{\lambda_p - \lambda_m}}$$

where $$\Delta = \lambda_p \lambda_m \left(\frac{(K_{eq} - K_o) - (T_{eq} - T_o)}{(A_o k_1 - K_o k_3) - (A_o k_2 - T_o k_4)}\right)$$

if $K_o = T_o = 0$ $$\Delta = \frac{\lambda_p \lambda_m}{A_o}\left(\frac{K_{eq} - T_{eq}}{k_1 - k_2}\right)$$

# initial concentration of the products

$$A \underset{k_3}{\overset{k_1}{\rightleftarrows}} K \qquad A \underset{k_4}{\overset{k_2}{\rightleftarrows}} T$$

$$\boxed{\mathrm{t_s} = \frac{\log\left(\frac{\lambda_\mathrm{p} - \Delta}{\lambda_\mathrm{m} - \Delta}\right)}{\lambda_\mathrm{p} - \lambda_\mathrm{m}}}$$

$$\Delta = \lambda_\mathrm{p}\lambda_\mathrm{m}\left(\frac{prodK - prodT}{rateK_{(t=0)} - rateT_{(t=0)}}\right)$$

$$prodK < prodT$$

$$rateK_{(t=0)} > rateT_{(t=0)}$$

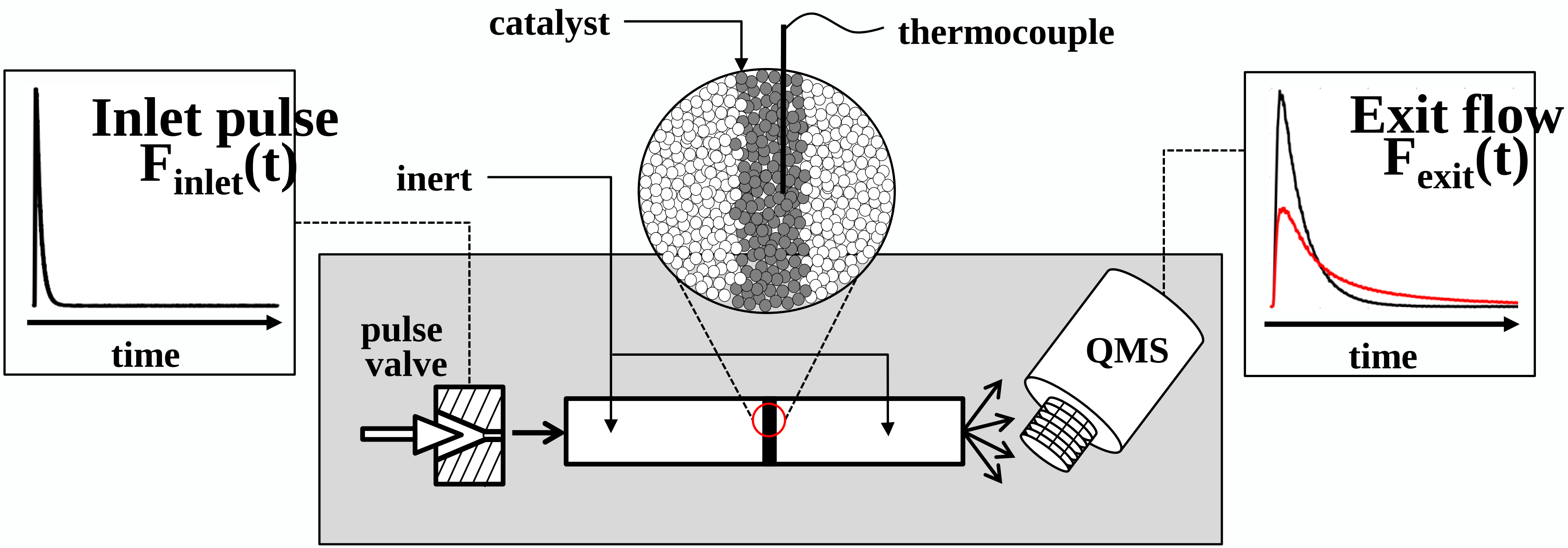
# conclusions

* The distinction between the kinetic and the thermodynamic control regimes should be made according to the rate of formation of the products. The kinetic control regime extends from the beginning of the reaction until the switching point; under this regime, the product with the largest rate of formation is the kinetic product. After the switching point, the thermodynamic control regime is settled, and now the thermodynamic product has the largest rate of formation.

* The value of the switching time ranges between zero and a maximum value $\dfrac{\log\left(\dfrac{\lambda_p}{\lambda_m}\right)}{\lambda_p - \lambda_m}$ ; after the switching time, occurs the maximum of concentration of the kinetic product, and eventually, the crossing of the concentration profiles of the competing products.

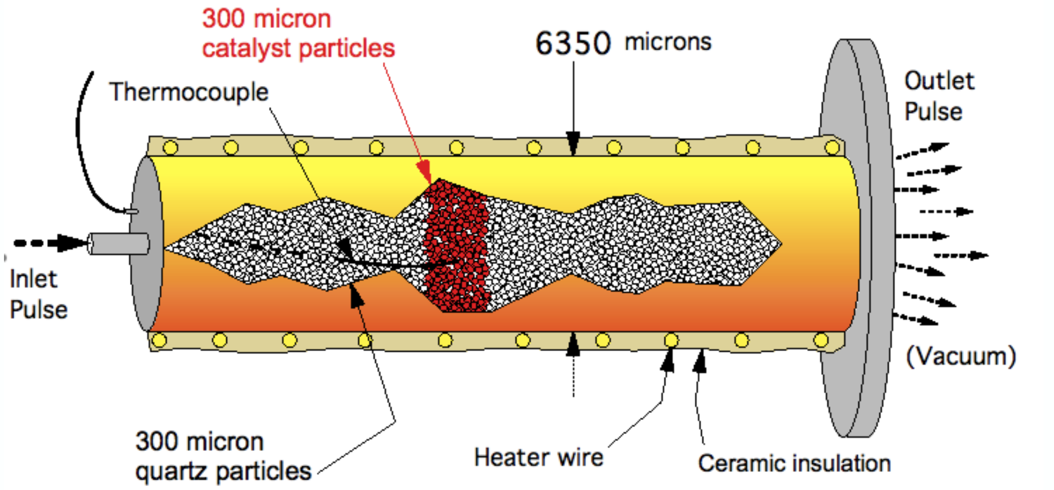
- III. Momentary Equlibrium

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

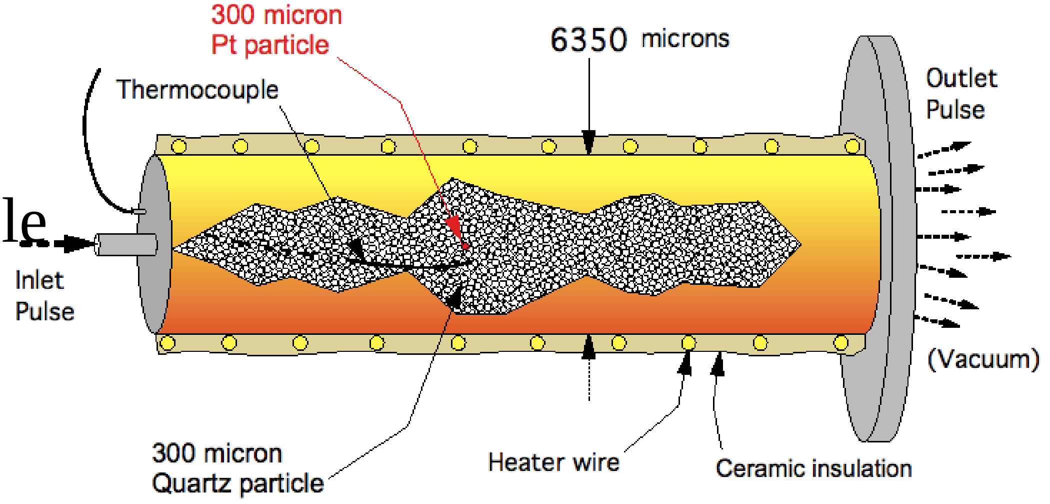


# Thin-zone and Single Particle Reactor Configurations

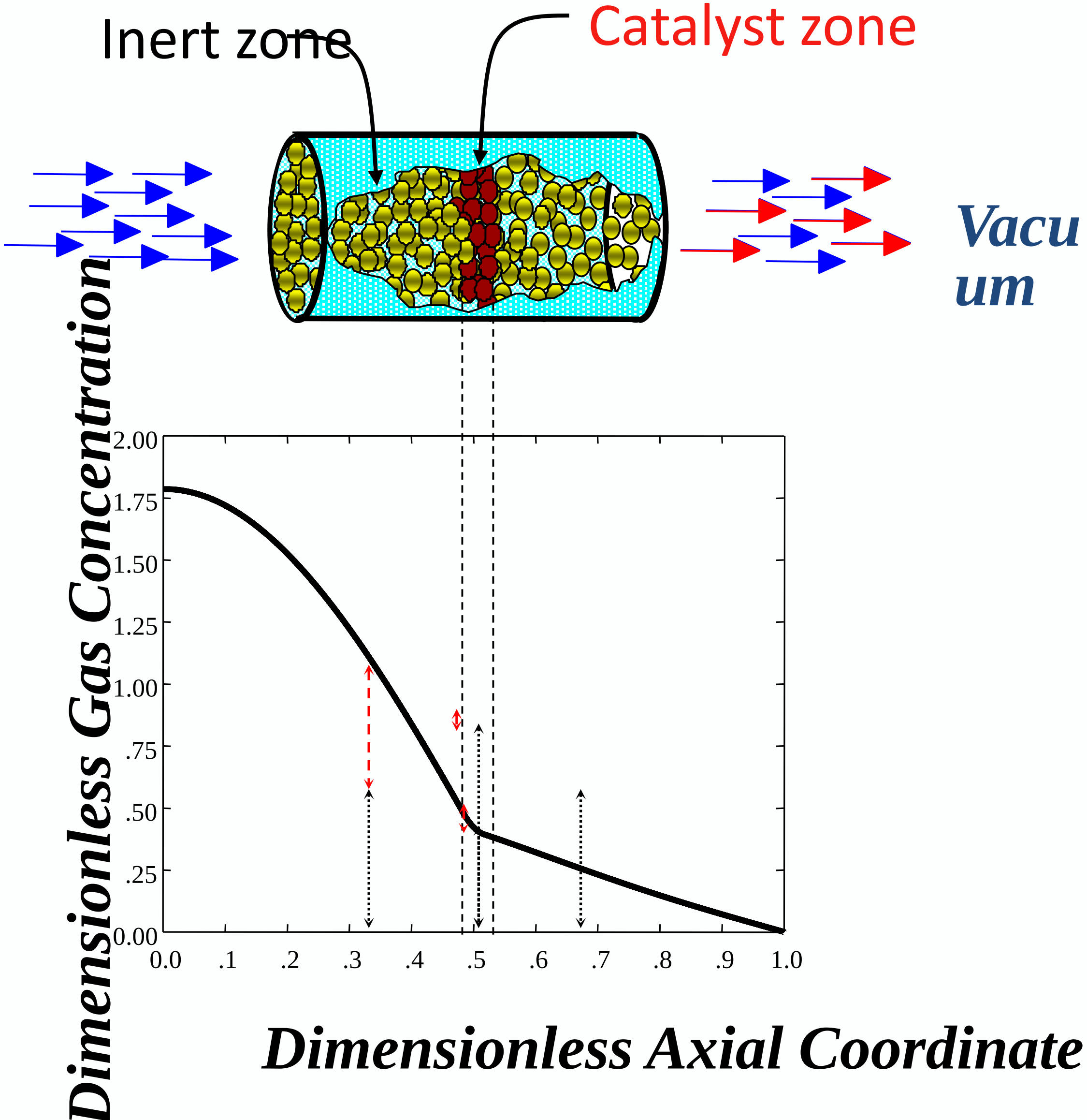
Thin-zone



Single-particle



# Thin-Zone TAP -Reactor (TZTR) Idea



Inert zone

Catalyst zone

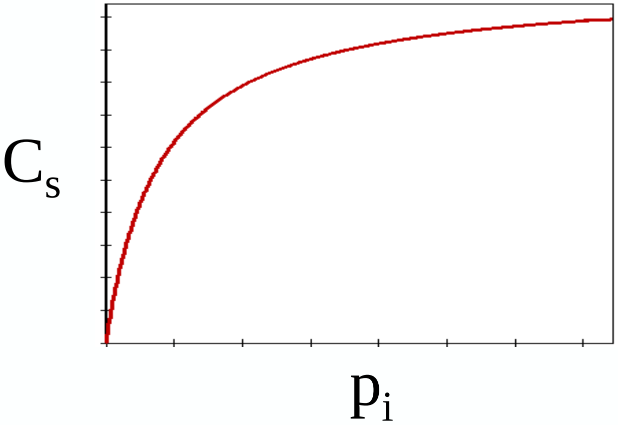
*Vacuum*

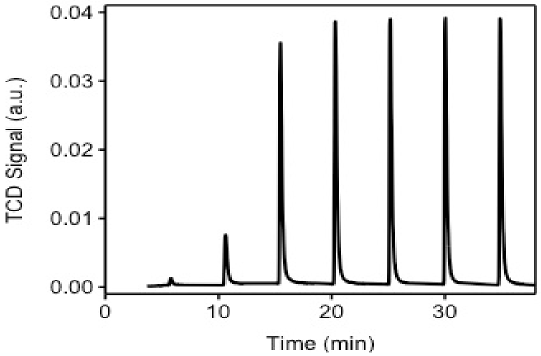
# Introduction

- **Adsorption equilibrium** is an essential step of catalytic processes, which is often used to measure the total concentration of catalytic sites.

- **The total concentration of sites** is typically determined by:

  - Very sensitive pressure and microbalance measurements in equilibrated closed system.
  - Chemisorption of irreversibly adsorbing molecules.
  - Chemisorption of reversibly adsorbing molecules at low temperatures (much less than operating).





# Introduction

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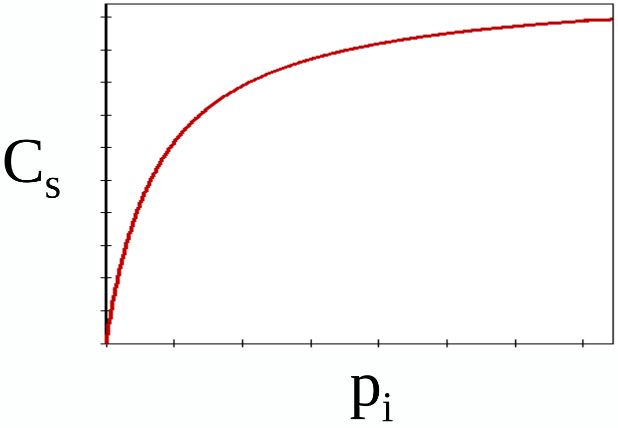

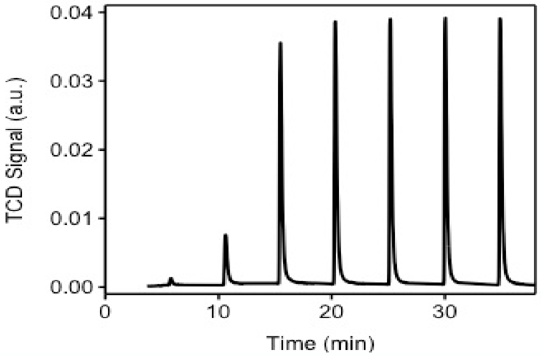

- Measuring the concentration of adsorption sites by **reversible chemisorption** under **realistic operating temperatures** and **non-steady-state conditions** presents a **significant challenge**.

# Outline

- 
- TAP experiments and data analysis
- Momentary Equilibrium
- Pulse-Intensity Modulation
- Experimental example
- Conclusions

# Outline

- Introduction
- TAP experiments and data analysis
- Momentary Equilibrium
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- Experimental example
- Conclusions

# Case study

## Single-site CO adsorption:

$$CO + Z \underset{k^+}{\overset{k^-}{\leftrightarrows}} ZCO \qquad K_{eq} = \frac{k^+}{k^-}$$

# Case study

## Single-site CO adsorption:

$$\mathrm{CO} + \mathrm{Z} \underset{k^{+}}{\overset{k^{-}}{\leftrightarrows}} \mathrm{ZCO} \qquad K_{eq} = \frac{k^{+}}{k^{-}}$$

- Kinetics is governed by

$$R_{CO} = -\frac{dC_{CO}}{dt} = k^{+}C_{Z}C_{CO} - k^{-}C_{ZCO} =$$

$$= \underline{k^{+}}(\underline{C_{Z,tot}} - C_{ZCO})C_{CO} - \underline{k^{-}}C_{ZCO}$$

# Case study

## Single-site CO adsorption:

$$\mathrm{CO} + \mathrm{Z} \underset{k^{+}}{\overset{k^{-}}{\leftrightarrows}} \mathrm{ZCO} \qquad\qquad K_{eq} = \frac{k^{+}}{k^{-}}$$

- Kinetics is governed by

$$R_{CO} = -\frac{dC_{CO}}{dt} = k^{+}C_{Z}C_{CO} - k^{-}C_{ZCO} =$$
$$= \underline{k^{+}}(\underline{C_{Z,tot}} - C_{ZCO})C_{CO} - \underline{k^{-}}C_{ZCO}$$

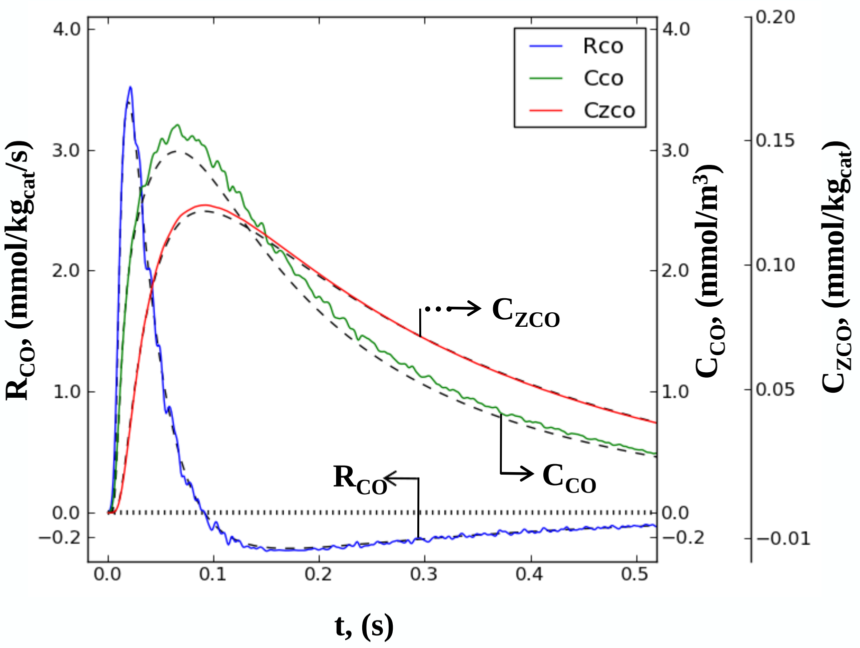
- Surface CO uptake can be obtained as

$$C_{ZCO}(t) = \int_{0}^{t} R_{CO}(t')dt'$$

We used numerical TZ TAP experiments with **realistic noise model** to elucidate kinetic behavior during CO adsorption in TAP.

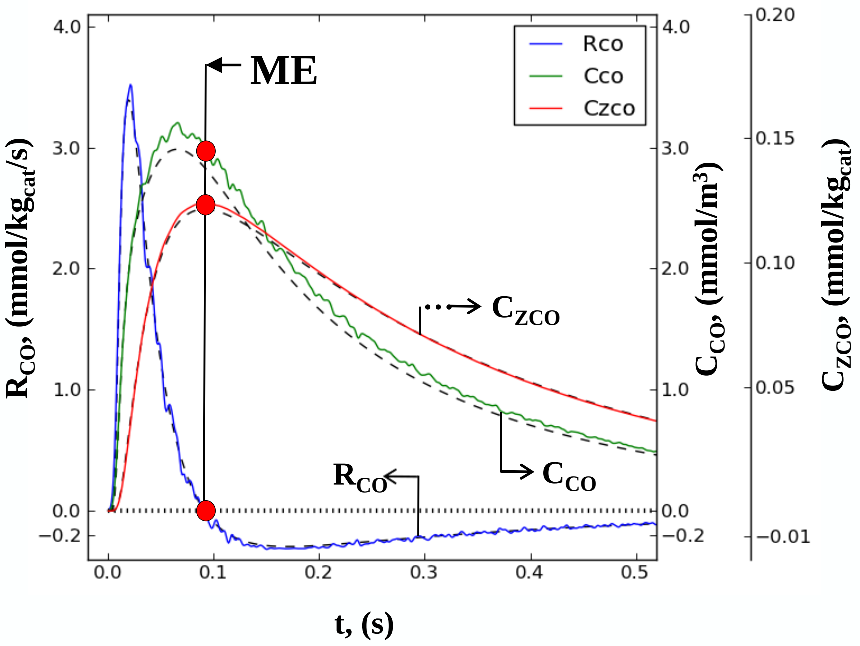
# Intra-pulse kinetic characteristics

Pulse-response experiment
in TZ TAP microreactor



# Momentary Equilibrium (ME)

Pulse-response experiment in TZ TAP microreactor



$$R_{CO}(t) = 0 \quad \rightarrow \quad r^{+} = r^{-}$$

# Momentary Equilibrium (ME)

Are the surface and gas concentrations in ME related via the **equilibrium constant**?

How do we use ME to obtain isotherms and estimate **the total concentration of sites**?

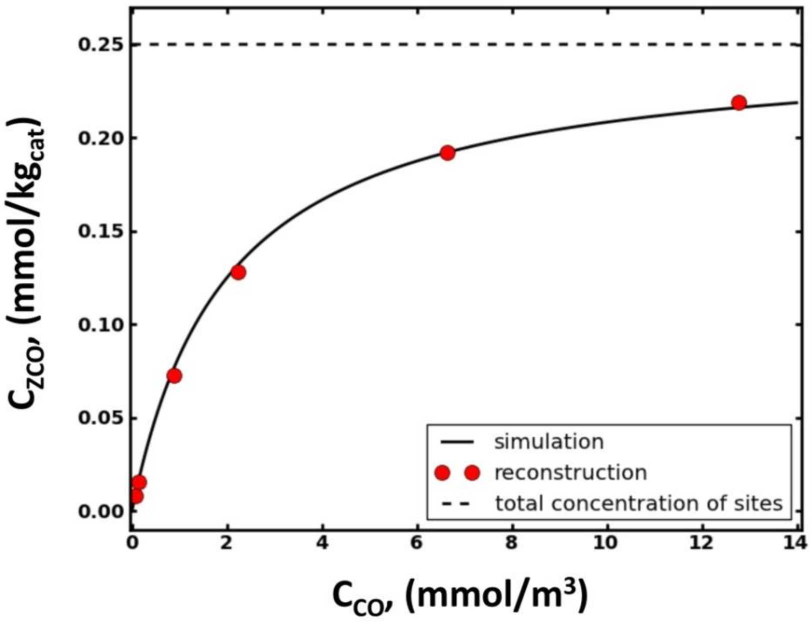
# Outline

- Introduction
- TAP experiments and data analysis
- Momentary Equilibrium
- **Pulse-Intensity Modulation**
- Experimental example
- Conclusions

# Pulse-Intensity Modulation

Langmuir isotherm:

$$C_{ZCO,ME} = \frac{K_{eq} C_{Z,tot} C_{CO,ME}}{1 + K_{eq} C_{CO,ME}}$$



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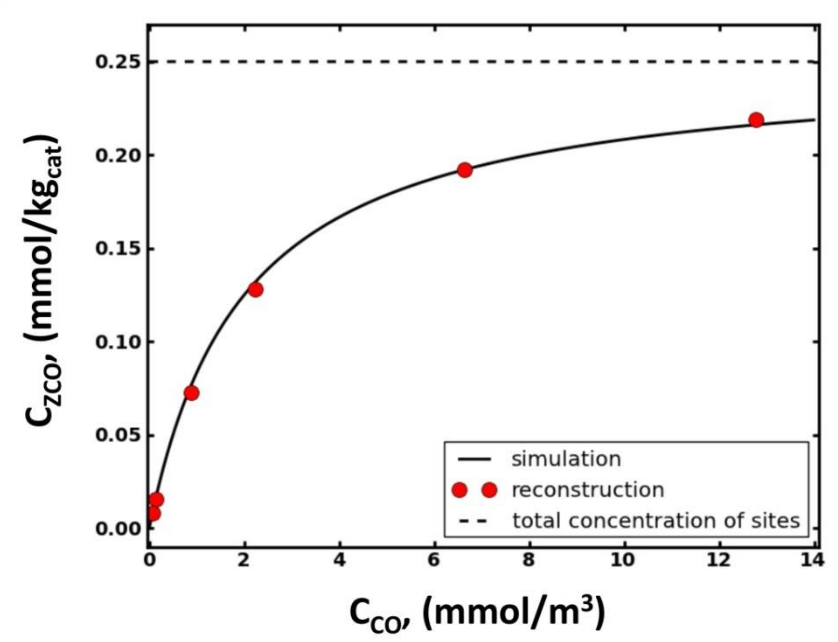
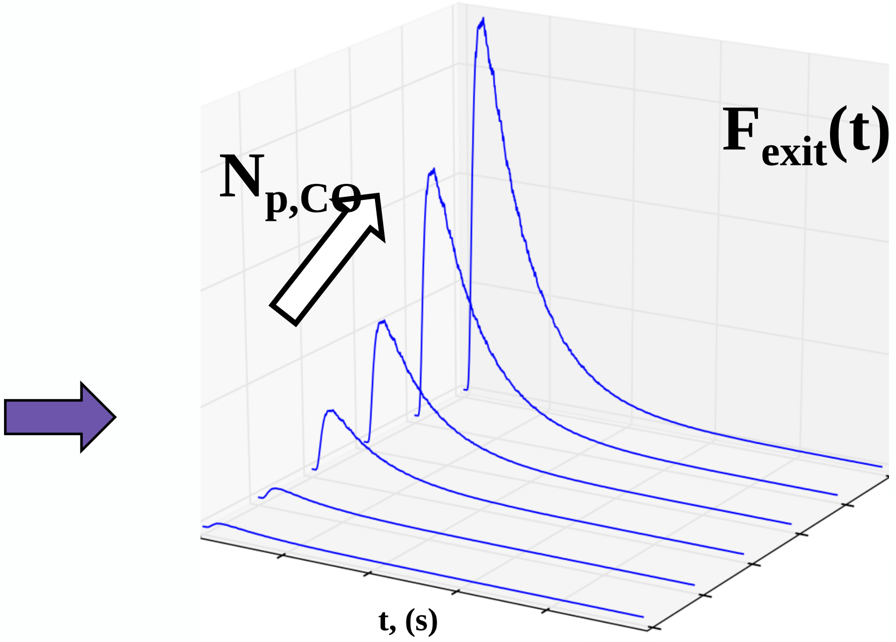




# Outline

- Introduction
- TAP experiments and data analysis
- Momentary Equilibrium
- Pulse-Intensity Modulation
- **Experimental example**
- Conclusions

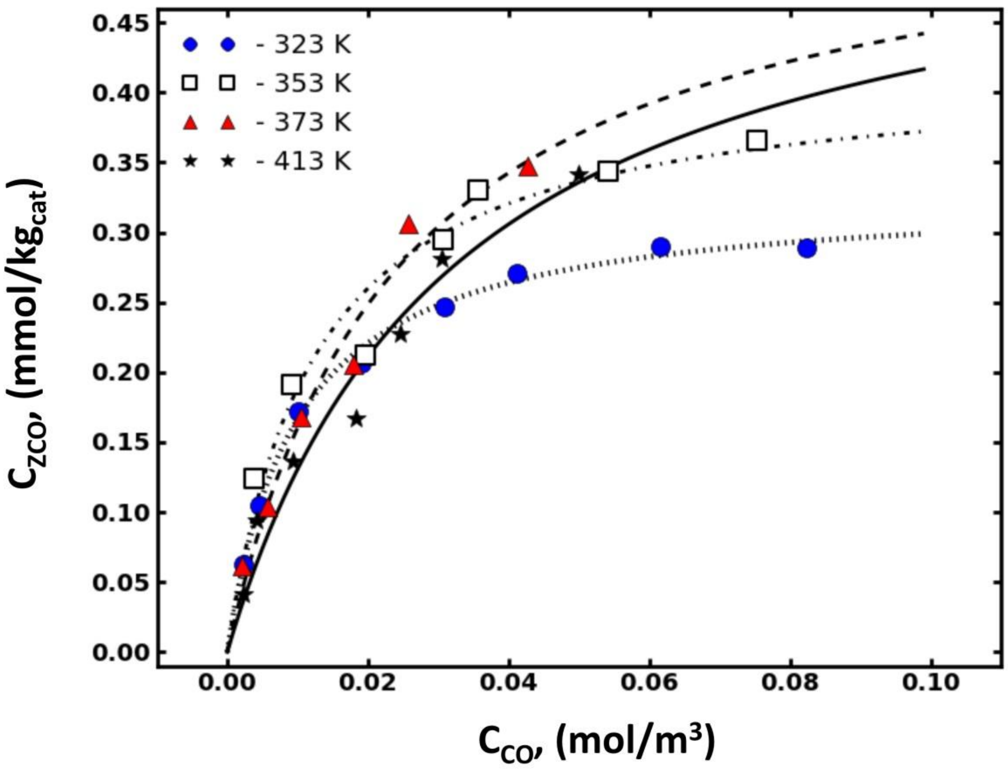
# Experimental example

**CO adsorption on $Pt/Mg(Al)O_x$ (1 wt. % Pt)**

Pulse-intensity range: $N_{p,CO} = 1 – 14.5 nmol_{CO}$

Temperature range: T = 50 – 140 °C

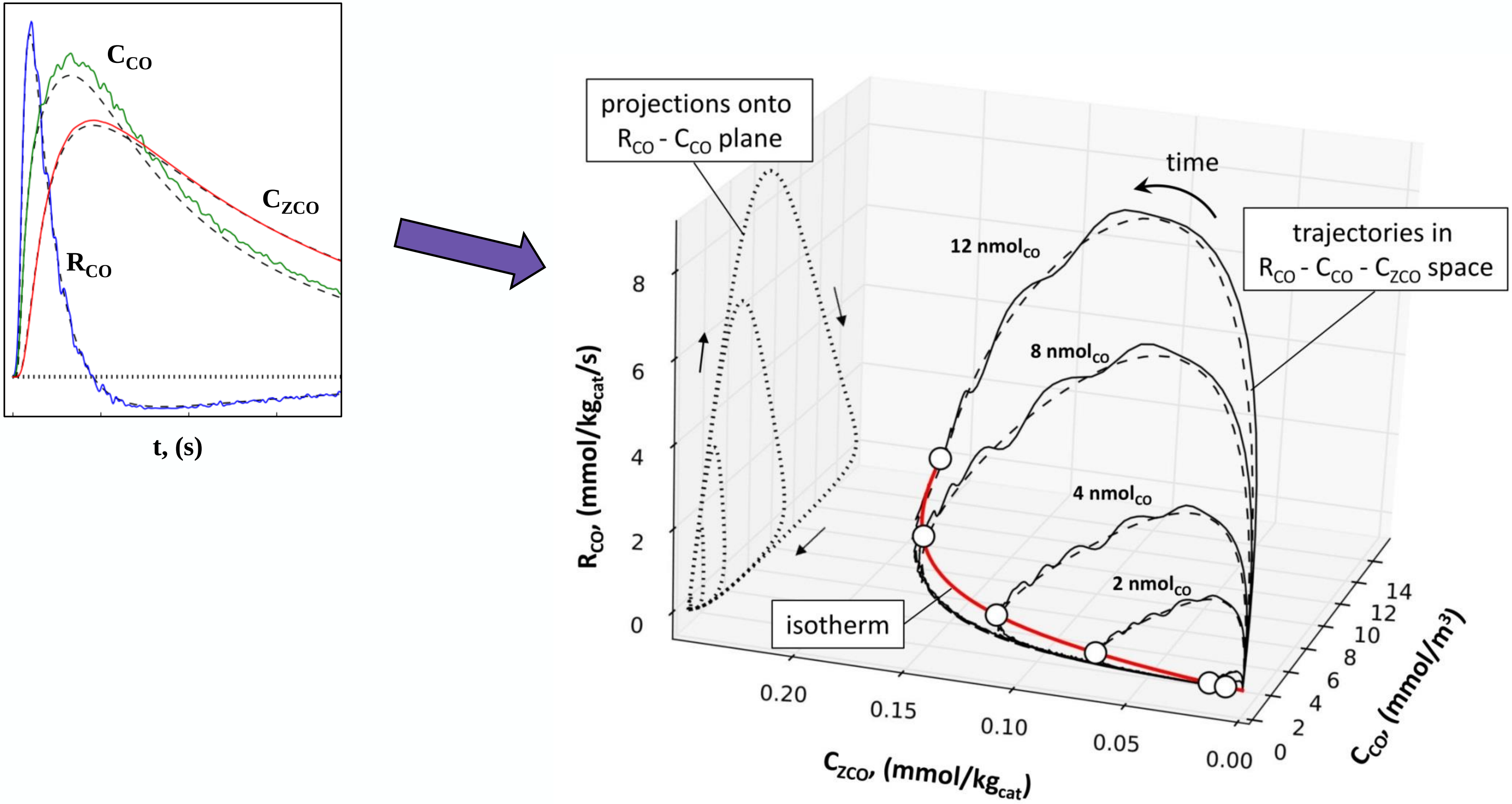
# Experimental example



Estimated concentration of adsorption sites: $C_{Z,tot}$ = 0.3-0.55 (mm

Estimated heat of CO adsorption: $\Delta H_{ads}$= - 17.9 (kJ/$mol_{CO}$)

# Rate-concentration trajectories



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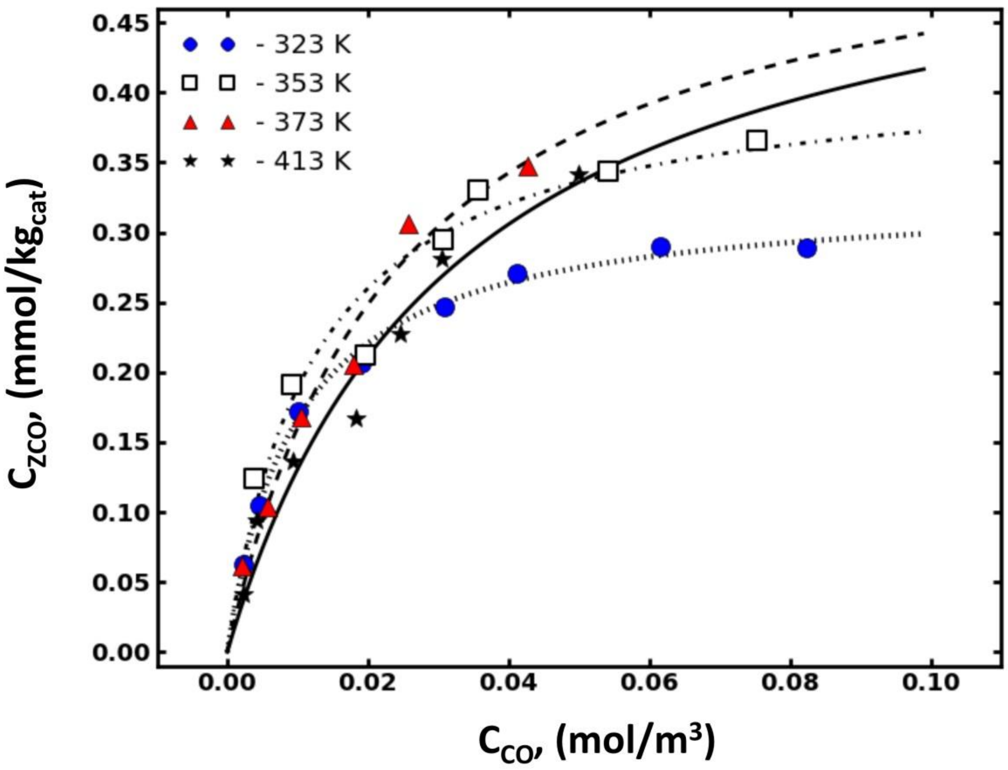

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# CONCLUSIONS

- **SIMPLE IS COMPLEX !**

# Acknowledgements

**John Gleaves**

**Alexander Gorban**

**Vladimir Galvita**

**Rebecca Fushimi**

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