Grasping Complexity in Chemical Kinetics

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In Memoriam Prof. Rutherford “Gus” Aris (1929-2005)
RUTHERFORD ARIS

• “TWO EYES ARE BETTER THAN ONE:
• some reflections on the importance to have more than one viewpoint in mathematical disciplines or other disciplines”,
TYPES OF COMPLEXITY

Simplicity | X-plicity
---|---
Ex-plicity | Complexity
Simplicity
Textbook Knowledge

• The main law of chemical kinetics is the Mass-Action Law

• The first-order reaction: \(A \Rightarrow B\) \(R = kC_a\)

• The second-order reaction: \(2A \Rightarrow B\) \(R = k(C)_a^2\)
  or \(A + B \Rightarrow C\) \(R = kC_aC_b\)

• The third-order reaction
  \(3A \Rightarrow B; R = k(C_a)^3;\)
  \(2A + B \Rightarrow C; R = k(C)_a^2C_b\)
Chemical Kinetics: Complexity

Textbook Knowledge

• 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) \( H_2 + O_2 = 2 \text{OH} \); 2) \( \text{OH} + H_2 = H_2O + H \); 3) \( H + O_2 = OH + O \);

4) \( O + H_2 = OH + H \); 5) \( O + H_2O = 2OH \); 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) \( O + O_2 + M = HO_2 + M \); 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) \( H + HO_2 = 2 \text{OH} \);

17) \( H + HO_2 = H_2O + O \); 18) \( H + HO_2 = H_2 + O_2 \); 19) \( O + HO_2 = OH + H \);

20) \( H + H_2O_2 = H_2O + OH \); 21) \( O + H_2O_2 = OH + HO_2 \); 22) \( H_2 + O_2 = H_2O + O \);

23) \( H_2 + O_2 + M = H_2O_2 + M \); 24) \( OH + M = O + H + M \); 25) \( HO_2 + OH = H_2O + O_2 \);

26) \( H_2 + O + M = H_2O + M \); 27) \( O + H_2O + M = H_2O_2 + M \); 28) \( O + H_2O_2 = H_2O + O_2 \);

29) \( H_2 + H_2O_2 = 2H_2O \); 30) \( H + HO_2 + M = H_2O_2 + M \)

• 5 intermediates: \( H^\cdot, O^\cdot, OH^\cdot, HO_2^\cdot, H_2O_2 \)

• 30 elementary steps
Problem:

Correspondence between observed kinetic behavior and “hidden” detailed mechanism

Three approaches:
1. Thermodynamically consistent “gray-box” approach
2. Non-steady-state kinetic screening (Chemical Calculus)
3. Analysis of kinetic fingerprints
Thermodynamically consistent “gray-box” approach,
or Ex-Plexity
Derivation of Steady-State Equations

Oxidation of SO\textsubscript{2}

(1) \[ \text{SO}_2 + V_2^{5+}O_2^{-} \rightleftharpoons V_2^{5+}O_2^{-} + \text{SO}_3 \]
(2) \[ \text{SO}_2 + V_2^{5+}O_2^{-} \rightleftharpoons V_2^{5+}\text{SO}_3^{2-} \]
(3) \[ \text{O}_2 + V_2^{5+}\text{SO}_3^{2-} \rightleftharpoons V_2^{5+}\text{O}_2^{-} + \text{SO}_3 \]

\[ 2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3 \]

\[
W = k_1^+ k_2^+ c_{\text{SO}_2}^2 + k_3^+ (k_1^+ + k_2^+) c_{\text{SO}_2} c_{\text{O}_2} + k_1^- k_3^- c_{\text{SO}_3}^2 + k_2^- (k_1^- + k_3^-) c_{\text{SO}_3} \\
+ k_1^+ k_2^- c_{\text{SO}_2} + k_2^+ k_3^- c_{\text{SO}_2} c_{\text{SO}_3} + k_3^+ k_1^- c_{\text{O}_2} c_{\text{SO}_3}
\]

\[
r = \frac{k_1^+ k_2^+ k_3^+ c_{\text{SO}_2}^2 c_{\text{O}_2} - k_1^- k_2^- k_3^- c_{\text{SO}_3}^2}{W} = \frac{c_{\text{SO}_2}^2 c_{\text{O}_2} - \frac{c_{\text{SO}_3}^2}{K_{\text{eq}}}}{\Omega_{\text{kin}}} \]

One-route catalytic reaction with the linear mechanism.

General expression (Yablonsky, Bykov, 1976)

\[ R = \frac{C_y}{\Sigma}, \]

where \( C_y \) is a “cyclic characteristics”,

\[ C_y = K^+ f^+(C) - K^- f^-(C), \]

\( C_y \) corresponds to the overall reaction;

\( \Sigma \) presents complexity of complex reaction;

\[ \Sigma = \sum \prod_K j^C j^i p^i \]
Graphs in Chemical Kinetics
• King and Altman: enzyme-catalyzed reactions: *linear reaction mechanisms*
• Intermediates are *nodes* of the graph
• Reactions are *edges*
• Graphs include *cycles*: finite sequences of graph edges with the same beginning and end node
• Present a graph of the complex reaction
• Write the weights, $W_j$, of all edges
• For every intermediate find the spanning tree by which it is produced from all others
• Find the weight of every spanning tree
• Find the sum of the weights of all spanning trees for the given node
• Find the total weight of all spanning trees of the graph:

$$W = \sum_{j=1}^{N_{\text{int}}} W_j$$
• “Simplicity” and “Complexity” are well known concepts

• What is ‘Ex-plexity’?
  
  It can be defined as a simplified “Complexity”, i.e. ‘Ex-Complexity’.

  Some kinetic polynomials, e.g. Langmuir-Hinshelwood equations, can be considered as examples of the ‘Ex-plexity’.
Ex-Plexity

- Ex-Plexity is a special behavior of complex systems which is similar to behavior of corresponding simple systems.
Kinetic resistance:

\[
\Omega_{\text{kin}} = \frac{W}{k^+} = \sum_l k_l \prod_i c_{\text{i}}^{p_{li}} = \frac{f^+(c_r) - f^-(c_p)}{K_{eq}}
\]

kinetic resistance = \frac{driving force}{steady-state reaction rate}

Analogy with Ohm’s law for electrical circuits:

resistance = \frac{voltage}{current}
What Kind of Kinetic Model?

Properties of Kinetic Resistance equation:

\[ \Omega_{\text{kin}} = \frac{f^+(c_r) - f^-(c_p)}{K_{\text{eq}}} \]

- \( \Omega_{\text{kin}} \) is an observable: both numerator and denominator can be measured or calculated from measured values (assuming \( K_{\text{eq}} \) is known)

\[ \Omega_{\text{kin}} = \sum_k \prod_i c_i^{p_{ki}} \]

- The equation is linear with respect to its parameters
Kinetic resistance, some questions:

• What is the link between the structure of the kinetic resistance and the detailed mechanism?
• Of how many terms does this resistance polynomial consist and what is its physicochemical meaning?
• Why are some of the terms of this polynomial sums of exponential functions?
• Are these terms mutually independent or not?
• Is it possible to find the parameters for the elementary reactions from the resistance polynomial and how?
Interpretation of the kinetic resistance terms (I)

- Kinetic resistance consist ‘forward’, ‘reverse’ and ‘mixed’ terms that include
  - (1) only reactant concentrations
  - (2) only products concentrations
  - (3) both reactant, and product concentrations.
- Rigorously, the first and second terms always presents in the rate expression
- The essential information on mechanism is reflected by the ‘mixed’ terms. Specific ‘mixed’ term indicates that in the mechanism there is an intermediate created by the reactant and product which are present in this term. It is not-trivial!
• Previous results have been obtained for the linear mechanisms with reaction which are linear regarding the intermediates.
• What to do with non-linear mechanisms?
Kinetic model of the adsorbed mechanism

(1) \[ 2 \text{K} + \text{O}_2 \Leftrightarrow 2 \text{KO} \]
(2) \[ \text{K} + \text{SO}_2 \Leftrightarrow \text{KSO}_2 \]
(3) \[ \text{KO} + \text{KSO}_2 \Leftrightarrow 2 \text{K} + \text{SO}_3 \]

• Steady state (or pseudo-steady-state) kinetic model is

• \[ \text{KO} : 2k_1 C_{\text{O}_2} (C_{\text{K}})^2 - 2k_{-1} (C_{\text{KO}})^2 - k_3 (C_{\text{KO}}) (C_{\text{KSO}_2}) + k_{-3} C_{\text{SO}_3} (C_{\text{K}})^2 = 0 ; \]

• \[ \text{KSO}_2 : k_2 C_{\text{SO}_2} C_{\text{K}} - k_{-2} (C_{\text{KSO}_2}) - k_3 (C_{\text{KO}}) (C_{\text{KSO}_2}) + k_{-3} C_{\text{SO}_3} (C_{\text{K}})^2 = 0 ; \]

• \[ C_{\text{K}} + C_{\text{KO}} + C_{\text{KSO}_2} = 1 \]
Our main result

• In the case of mass-action-law model, it is always possible to reduce our polynomial algebraic system to a polynomial of only variable, steady-state reaction rate.

• For this purpose, an analytic technique of variable elimination is used. Computer technique of elimination is used as well.

• Mathematically, the obtained polynomial is a system resultant. We term it a kinetic polynomial.
Kinetic Polynomial
(Lazman-Yablonsky)

\[
\left( \sum \prod_{j_L} K_{j_L i} C_{i}^{m_i, j_L} \right) R^L + \ldots + \left( \sum \prod_{j_1} K_{j_1 i} C_{i}^{m_i, j_1} \right) R + \\
+ B_0 \left( K^+ f^+ (C) - K^- f^- (C) \right) = 0
\]
Four-term rate equation

- Thermodynamic branch of the kinetic polynomial

\[ R = \frac{k f c - K_{eq}^{-1} f - c}{\sum N k, c} \]
Conclusion: A New Strategy:

- (1) Calculate the kinetic resistance based on the reaction net-rate and its driving force;
- (2) Present this resistance as a function of concentrations and temperature on both sides of the equilibrium.

An advantage of this procedure is that the kinetic resistance is just a linear polynomial regarding its parameters in difference from the non-linear LHHW-kinetic models.
Reverse and forward water-gas shift reaction

\[ \text{H}_2 + \text{CO}_2 = \text{H}_2\text{O} + \text{CO} \]  
Kin. Resist. vs Pco

![Graph showing the relationship between KR (mmol/m³·s·(mmol kg⁻¹·s⁻¹)) and Partial pressure CO (kPa)]
Ln(Kin.Res) vs (1/T)
Evolution of kinetic behavior of the complex reversible reaction with the increase of parameter (concentration)

Typical scenario: from the “close to equilibrium”-domain to the “far from equilibrium”-domain

- “Close to Equilibrium”- Domain. Kinetic behavior in accordance with the overall reaction
- Domain of Limitation by the controlled parameter
- Domain(s) of Limitation by the other concentrations (or intermediates)
- Domain of Irreversibility (“Far from Equilibrium”)
- Domain(s) of Critical Phenomena (“Far from Equilibrium”), e.g. multiplicity of steady states
• All this analysis has been done based on the Kinetic Polynomial concept
• CHEMICAL CALCULUS
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 → “chemical calculus”
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)
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.
Founders of infinitesimal calculus: Newton and Leibnitz
Isaac Newton (1743-1727)
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 calculus in chemistry: 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)
TAP Reactor System - Overview

- Continuous flow valve
- Pulse valve
- Microreactor
- Reactant mixture
- Catalyst
- Mass spectrometer
- Vacuum (10⁻⁸ torr)
- Exit flow (F_A)

Graphs showing:
- Inert flow over time
- Reactant flow over time
- Product flow over time
TAP Multipulse Experiment Combines
State-Defining & State-Altering Experiment

Inert

Reactant

Product

State-defining Experiment

Insignificant change

State-altering Experiment

Small number of pulses

Large number of pulses
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
Experimental and Predicted Responses
Argon Pulsed over Quartz Particles

Experimental and Predicted Responses
Argon and Butane Pulsed over VPO

Non-uniformity along the catalyst bed was produced in multi-pulse 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
Thin Zone TAP experiments
Thin-zone and Single Particle Reactor Configurations

Thin-zone

Single-particle
Thin-Zone TAP-Reactors (TZTR) Idea

- Inert zone
- Catalyst zone
- Dimensionless Axial Coordinate
- Dimensionless Gas Concentration

Graph showing the distribution of gas concentration along the dimensionless axial coordinate.
One zone: the diffusion equation requires an initial condition and two boundary conditions (as a second order PDE)

Transport equation (Knudsen diffusion)

\[
\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}
\]

Initial Pulse (Dirac delta)

\[C(x,0) = \delta_{x=0}\]

Boundary Conditions

\[-D \frac{\partial C}{\partial x}(0,t) = 0\]

\[-D \frac{\partial C}{\partial x}(L,t) = 0\]

Observation (molecular flux)

\[F = -D \frac{\partial C}{\partial x}(L,t)\]

\[C(L, t) = 0\]

Closed valve

Vacuum
Two zones: each zone requires two boundary conditions

Transport equation (Knudsen diffusion)
\[
\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}
\]

Initial Pulse (Dirac delta)
\[
C(x,0) = \delta_{x=0}
\]

Boundary Conditions
\[
-D \frac{\partial C}{\partial x}(0,t) = 0
\]
\[
C_1 = C_II = C
\]
\[
D \frac{\partial C_1}{\partial x} + D \frac{\partial C_{II}}{\partial x} = R(C, N_z)
\]
\[
\frac{dN_z}{dt} = R(C, N_z)
\]
\[
C(L,t) = 0
\]

Observation (molecular flux)
\[
F = -D \frac{\partial C}{\partial x}(L,t)
\]

Closed valve
Concentration continuity
TZ gas phase balance
TZ surface balance
Vacuum

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

\[ C_s(t) = Uptake(t) - Release(t) = \int_0^t \sum_i v_i R_i(\tau) d\tau \]
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?

Decoding complex mechanisms:

Classical problem – Langmuir-Hinshelwood or Eley-Rideal?

<table>
<thead>
<tr>
<th>Elementary step</th>
<th>Reaction rate</th>
</tr>
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<tbody>
<tr>
<td>(1) $O_2 + 2Z \rightarrow 2ZO$</td>
<td>$r_1 = k_1^+ C_Z^2 C_{O_2}$</td>
</tr>
<tr>
<td>(2) $CO + Z \rightleftharpoons ZCO$</td>
<td>$r_2 = k_2^+ C_Z C_{CO} - k_2^- C_{ZCO}$</td>
</tr>
<tr>
<td>(3) $ZO + CO \rightarrow Z + CO_2$</td>
<td>$r_3 = k_3^+ C_{ZO} C_{CO}$</td>
</tr>
<tr>
<td>(4) $ZO + ZCO \rightarrow 2Z + CO_2$</td>
<td>$r_4 = k_4^+ C_{ZO} C_{ZCO}$</td>
</tr>
</tbody>
</table>

For any combination of elementary steps, surface uptakes of CO and oxygen can be calculated as:

$$C_{ZCO}(t) = \int_0^t (R_{CO}(\tau) - R_{CO_2}(\tau)) d\tau$$

$$C_{ZO}(t) = \int_0^t (2R_{O_2}(\tau) - R_{CO_2}(\tau)) d\tau$$
Step 1: Directly comparing rates in a state-defining experiment
Step 2: Testing coherency of the entire data set (time invariant parameters)

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<td>(ZO + CO \rightarrow Z + CO_2)</td>
<td>(r_3 = k_3^+ C_Z O C_{CO})</td>
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<td>(ZO + ZCO \rightarrow 2Z + CO_2)</td>
<td>(r_4 = k_4^+ C_Z O C_{ZCO})</td>
</tr>
</tbody>
</table>

Apparent kinetic parameters:

\[
k_3^+ = \frac{R_{CO_2}(t)}{C_{ZO}(t) C_{CO}(t)}
\]

\[
k_4^+ = \frac{R_{CO_2}(t)}{C_{ZO}(t) C_{ZCO}(t)}
\]
Step 2: Decision tree for oxygen pre-covered surface

Legend:

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

Testing rates

Testing parameters
KINETIC FINGERPRINTS
Analysis of Kinetic Fingerprint

Aim:
To find features and characteristics of observed kinetic behavior to resolve the detailed mechanism

Example

Consecutive: 
\[ A \rightarrow B \rightarrow C \]

Parallel:
\[ A \leftrightarrow B \leftrightarrow C \]

Maximum in \( c_B \) is a fingerprint of the consecutive mechanism
Aim:
To find features and characteristics of observed kinetic behavior to resolve the detailed mechanism

Example

Consecutive: $\text{A} \rightarrow \text{B} \rightarrow \text{C}$

Parallel: $\text{A} \leftrightarrow \text{B} \leftrightarrow \text{C}$

maximum in $c_B$ is a fingerprint of the consecutive mechanism
Critical Phenomena in Heterogeneous Catalytic Kinetics (Fingerprint of Mechanism):

Multiplicity of Steady-States in Catalytic Oxidation
(CO oxidation over Platinum)
NON-LINEAR FINGERPRINT

• Multiplicity of steady states is a fingerprint of the special non-linear mechanism, i.e. the mechanism in which there is an interaction between different intermediates (surface intermediates). It was proven rigorously for mass-action-law kinetics. Example of this mechanism is 3-step mechanism of CO adsorption on Pt
Kinetics 2.0 : New Patterns of Kinetic Behavior: Intersections, Coincidences and Reciprocal Time Invariances
‘X-PLICITY’

- What is ‘X-plicity’?
- Some unknown surprising properties of ‘simple’ systems
- Examples;
  1. Dual Kinetic Experiment (DKE): Equilibrium relationships between non-equilibrium dependences
  2. Coincidences in linear chemical systems
Reversible reactions

\[
\begin{align*}
    \frac{k_1}{k_{-1}} & \quad \text{Batch reactor, } A & B \\
    \text{from } (1,0) & \quad \text{from } (0,1) \\
\end{align*}
\]

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

\[
\begin{align*}
    \mathcal{L}B_A(s) &= \frac{k_1}{s^2 + (k_1 + k_{-1})s} \\
    \mathcal{L}A_B(s) &= \frac{k_{-1}}{s^2 + (k_1 + k_{-1})s}
\end{align*}
\]

Laplace domain solution

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

\[ K_{eq} = \frac{k_1^+}{k_1^-} = \frac{C_{BA}(t)}{C_{AB}(t)} \]
Reversible consecutive reactions

Next case: batch reactor, \( A \xrightarrow{k_1} B \xleftarrow{k_{-1}} C \)

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

Actually, \( t_{BA_{\max}} \equiv t_{AB_{\max}}? \)

\[
\frac{B_A(t)}{A_B(t)} = \frac{k_1}{k_{-1}} = K_{eq} \text{ is constant!}
\]

\[
\mathcal{L}B_A(s) = \frac{k_1}{s^2 + (k_1 + k_{-1} + k_2)s + k_1k_2} \quad \mathcal{L}A_B(s) = \frac{k_{-1}}{s^2 + (k_1 + k_{-1} + k_2)s + k_1k_2}
\]

A ⇌ B → 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) $C_{A,0} = 0$, $C_{B,0} = 1$. 
Model reaction

Consider a simple reaction \( A \rightleftharpoons B \rightarrow C \) in a batch reactor with kinetics governed by the following system of linear ODEs:

\[
\begin{align*}
\frac{dC_A(t)}{dt} &= -k_1^+ C_A(t) + k_1^- C_B(t) \\
\frac{dC_B(t)}{dt} &= k_1^+ C_A(t) - (k_1^- + k_2^+) C_B(t) \\
\frac{dC_C(t)}{dt} &= k_2^+ C_B(t)
\end{align*}
\]
Constant reciprocal ratio

Nonzero eq. concentrations: $A \xleftrightarrow{k_{-1}} B \xleftrightarrow{\varepsilon>0} C$

Detailed equilibrium: $k_{A\rightarrow B} A_{\text{eq}} = k_{B\rightarrow A} B_{\text{eq}}$

$$\frac{k_{A\rightarrow B}}{k_{B\rightarrow A}} = \frac{B_{\text{eq}}}{A_{\text{eq}}}$$

Matrix $K$, $K_{ij} = -k_{A_j\rightarrow A_i}$, dgl. $K_{ii} = \sum k_{A_i\rightarrow A_j}$,

self-adjoint w.r.t. weighted quadratic $W = \sum_i \frac{A_i^2}{A_{i,\text{eq}}}$
General time-invariances

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

• We have also extended it to the TAP (Temporal Analysis of Products) reactor.
Rigorous proof by Gorban

• For linear or linearized kinetics with microreversibility, $dx/dt = Kx$, the kinetic operator $K$ is symmetric in the entropic product. This form of Onsager reciprocal relations implies 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
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.

Example: Euler point,
\[ k_1 = k_2 = 1 \text{ s}^{-1}, \quad k_1^- = 0 \text{ s}^{-1} \]
\[ t_{B,\text{max}} = 1 \text{ s} \]
\[ C_{A,\text{intersect}} = C_{B,\text{intersect}} = 1/e \]
A. Coincidences

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

\[
\frac{dC_A}{dt} = -k_1 C_A,
\]

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

\[
\frac{dC_C}{dt} = k_2 C_B,
\]
Coincidences (cont’d)

- Solutions (known before)

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

\[
C_B(t) = C_{A,0} k_1 \frac{\exp(-k_1 t) - \exp(-k_2 t)}{k_2 - k_1} + C_{B,0} \exp(-k_2 t),
\]

\[
C_C(t) = C_{A,0} \left[ 1 - \frac{k_2 \exp(-k_1 t) - k_1 \exp(-k_2 t)}{k_2 - k_1} \right] + C_{B,0} (1 - \exp(-k_2 t))
\]
Coincidences (cont’d)

• New 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.
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.
• Each point has special ordering or behavior.
Coincidences (cont’d)

• Acme, $k_2 = k_1/2$
Coincidences (cont’d)

- Lambert, $k_2 = 1.1739... \ k_1$
Consecutive reactions

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.
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.

- ($\triangle$) $t_1 < t_2$,
- ($\blacktriangle$) $t_1 > t_2$,
- ($\blacktriangledown$) only $t_1$ exists,
- ($\blacklozenge$) only $t_2$ exists,
- ($\blacklozenge$) no intersections
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):
The most impressive coincidence in my life
RUTHERFORD ARIS

• “TWO EYES ARE BETTER THAN ONE:
  • some reflections on the importance to have more than one viewpoint in mathematical disciplines or other disciplines”,
‘X-PLICITY’

• What is ‘X-plicity’?
• Some unknown surprising properties of ‘simple’ systems
• Examples;
  (1) Dual Kinetic Experiment (DKE): Equilibrium relationships between non-equilibrium dependences
  (2) Coincidences in linear chemical systems
Simplicity, Complexity, Ex-Plexity, X-Plicity...
TYPES OF COMPLEXITY

Simplicity  X-plicity

Ex-plicity  Complexity
Ex-Plexity

- Ex-Plexity is a special behavior of complex systems which is similar to behavior of corresponding simple systems.
X-Plicity

• X-Plicity is a special property of simple systems which is characterized by a high level of complexity
Elementary, Watson....
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References


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CONCLUSIONS

– NO CONCLUSIONS!
• BACK TO HISTORY...
• BACK TO CELEBRITIES...
Isaac Newton (1642-1726)
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 calculus in chemistry:  
John T. Gleaves (1946- )
“It has seen further it is by standing on the shoulders of giants”
(Isaac Newton, Letter to Robert Hook, February 1676)
Gregory S. Yablonsky (?)
THANK YOU
FOR YOUR ATTENTIVE PATIENCE!
“I gave my mind a thorough rest by plunging into a chemical analysis”
(Sherlock Holmes, “The Sign of Four”, Chapter 10)
Leaning Tower of Pisa
The Tower of Babel