# Reciprocal relations between kinetic curves

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**Abstract** – We study coupled irreversible processes. For linear or linearized kinetics with microreversibility, $\dot{x} = Kx$, the kinetic operator $K$ is symmetric in the entropic inner product. This form of Onsager's reciprocal relations implies that the shift in time, $\exp(Kt)$, is also a symmetric operator. This generates the reciprocity relations between the kinetic curves. For example, for the Master equation, if we start the process from the $i$-th pure state and measure the probability $p_j(t)$ of the $j$-th state ($j \neq i$), and, similarly, measure $p_i(t)$ for the process, which starts at the $j$-th pure state, then the ratio of these two probabilities $p_j(t)/p_i(t)$ is constant in time and coincides with the ratio of the equilibrium probabilities. We study similar and more general reciprocal relations between the kinetic curves. The experimental evidence provided as an example is from the reversible water gas shift reaction over iron oxide catalyst. The experimental data are obtained using Temporal Analysis of Products (TAP) pulse-response studies. These offer excellent confirmation within the experimental error.

## Introduction. –

*A bit of history.* In 1931, L. Onsager [1,2] gave the backgrounds and generalizations to the reciprocal relations introduced in 19th century by Lord Kelvin and H. v. Helmholtz. In his seminal papers, L. Onsager mentioned also the close connection between these relations and the *detailed balancing* of elementary processes: at equilibrium, each elementary transaction should be equilibrated by its inverse transaction. This principle of detailed balance was known long before for the Boltzmann equation [3]. A. Einstein used this principle for the linear kinetics of emission and absorption of radiation [4]. In 1901, R. Wegscheider published an analysis of detailed balance for chemical kinetics [5].

The connections between the detailed balancing and Onsager's reciprocal relations were clarified in detail by N. G. v. Kampen [6]. They were also extended for various types of coordinate transformations which may include time derivatives and integration in time [7]. Recently [8], the reciprocal relations were derived for nonlinear coupled transport processes between reservoirs coupled at mesoscopic contact points. Now, an elegant geometric

framework is elaborated for Onsager's relations and their generalizations [9].

Onsager's relations are widely used for extraction of kinetic information about reciprocal processes from experiments and for the validation of such information (see, for example, [10]): one can measure how process $A$ affects process $B$ and extract the reciprocal information, how $B$ affects $A$.

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 [11]. 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".

According to Onsager's work [1], the fluxes in chemical kinetics are time derivatives of the concentrations and potentials are expressed through the chemical potentials. The fluxes (near equilibrium) are linear functions of potentials and the reciprocal relations state that the

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coefficient matrix of these functions is symmetric. It is impossible to measure these coefficients directly. To find them one has to solve the inverse problem of chemical kinetics. This problem is often ill-posed.

Such a difficulty, appearance of ill-posed problems in the verification of the reciprocal relations, is typical because these relations connect the kinetic coefficients. Sometimes it is possible to find them directly in separate experiments but if it is impossible then the inverse problem arises with all the typical difficulties.

In our work we, in particular, demonstrate how it is possible to verify the reciprocal relations without the differentiation of the empiric kinetic curves and solving the inverse problems, and present the experimental results which demonstrate these relations for one reaction kinetic system. For this purpose, we have to formulate the reciprocal relations directly between the measurable quantities.

These reciprocal relations between kinetic curves use the symmetry of the propagator in the special entropic inner product. A dual experiment is defined for each ideal kinetic experiment. For this dual experiment, both the initial data and the observables are different (they exchange their positions), but the results of the measurement is essentially the same function of time.

*The structure of the paper.* We start from the classical Onsager relations and reformulate them as conditions on the kinetic operator $K$ for linear or linearized kinetic equations $\dot{x} = Kx$. This operator should be symmetric in the entropic inner product, whereas the matrix $L$ that transforms forces into fluxes should be symmetric in the standard inner product, *i.e.* $L_{ij} = L_{ji}$. The form of reciprocal relations with special inner product is well known in chemical and Boltzmann kinetics [12,13]. They are usually proved directly from the detailed balance conditions. Such relations are also universal just as the classical relations are.

Real functions of symmetric operators are also symmetric. In particular, the propagator $\exp(Kt)$ is symmetric. Therefore, we can formulate the reciprocal relation between kinetic curves. These relations do not include fluxes and time derivatives, hence, they are more robust. We formulate them as the symmetry relations between the observables and initial data (the *observables–initial-data symmetry*).

A particular case of this symmetry for a network of monomolecular chemical reactions or for the Master equation, which describe systems with detailed balance, seems rather unexpected. Let us consider two situations for a linear reaction network.

1. The process starts at the state "everything is in $A_q$", and we measure the concentration of $A_r$. The result is $c_r^a(t)$ ("how much $A_r$ is produced from the initial $A_q$").

2. The process starts at the state "everything is in $A_r$", and we measure the concentration of $A_q$. The result

is $c_q^b(t)$ ("how much $A_q$ is produced from the initial $A_r$") (the *dual experiment*).

The results of the dual experiments are connected by the identity

$$\frac{c_r^a(t)}{c_r^{\mathrm{eq}}} \equiv \frac{c_q^b(t)}{c_q^{\mathrm{eq}}} \, ,$$

where $c$ are concentrations and $c^{\mathrm{eq}}$ are equilibrium concentrations.

The symmetry with respect to the observables–initial-data exchange gives the general rule for production of the reciprocal relations between kinetic curves.

Many real processes in chemical engineering and biochemistry include irreversible reactions, *i.e.* the reactions with a negligible (zero) rate of the reverse reaction. For these processes, the microreversibility conditions and the backgrounds of classical Onsager relations are not applicable directly. Nevertheless, they may be considered as limits of systems with microreversibility when some of the rate constants for inverse reactions tend to zero. We introduce the correspondent weak form of detailed balance, formulate the necessary and sufficient algebraic conditions for this form of detailed balance and formulate the observables–initial-data symmetry for these systems.

The experimental evidence of the observables–initial-data symmetry is presented for the reversible water gas shift reaction over iron oxide catalyst. The experimental data are obtained using Temporal Analysis of Products (TAP) pulse-response studies. These offer excellent confirmation within experimental error.

**Two forms of the reciprocal relations: forces, fluxes and entropic inner product.** – Let us consider linear kinetic equations or kinetic equations linearized near an equilibrium $x^{\mathrm{eq}}$ (sometimes, it may be convenient to move the origin to $x^{\mathrm{eq}}$):

$$\dot{x} = Kx. \tag{1}$$

In the original form of Onsager's relations, the vector of fluxes $J$ and the vector of thermodynamic forces $X$ are connected by a symmetric matrix, $J = LX$, $L_{ij} = L_{ji}$. The vector $X$ is the gradient of the corresponding thermodynamic potential: $X_i = \partial\Phi/\partial x_i$. For isolated systems, $\Phi$ is the entropy. For other conditions, other thermodynamic potentials are used. For example, for the constant volume $V$ and temperature $T$ conditions, $\Phi$ is $-F/T$ and for the constant pressure $P$ and temperature conditions, $\Phi$ is $-G/T$, where $F$ is the Helmholtz energy (free energy) and $G$ is the Gibbs energy (free enthalpy). These *free entropy* functions are also known as the Massieu-Planck potentials [14]. Usually, they are *concave*.

For the finite-dimensional systems, like chemical kinetics or the Master equation, the dynamics satisfy the linear (linearized) kinetic equation $\dot{x} = Kx$, where

$$K_{ij} = \sum_l L_{il} \left. \frac{\partial^2 \Phi}{\partial x_l \partial x_j} \right|_{x^{\mathrm{eq}}} , \ \ i.e. \ \ K = L(D^2\Phi)_{x^{\mathrm{eq}}}.$$

This matrix is not symmetric but the product $(D^2\Phi)_{x^{\mathrm{eq}}} K = (D^2\Phi)_{x^{\mathrm{eq}}} L (D^2\Phi)_{x^{\mathrm{eq}}}$ is already symmetric, hence, $K$ is symmetric (self-adjoint) in the entropic scalar product

$$\langle a \,|\, Kb \rangle_\Phi \equiv \langle Ka \,|\, b \rangle_\Phi, \tag{2}$$

where

$$\langle a \,|\, b \rangle_\Phi = -\sum_{ij} a_i \left.\frac{\partial^2\Phi}{\partial x_l \partial x_j}\right|_{x^{\mathrm{eq}}} b_j. \tag{3}$$

Further on, we use the angular brackets for the entropic inner product (3) and its generalizations and omit the subscript $\Phi$.

For the spatially distributed systems with transport processes, the variables $x_i$ are functions of the space coordinates $\xi$, the equations of divergence form appear, $\partial_t x_i = -\nabla_\xi \cdot J_i$, thermodynamic forces include also gradients in space variables, $X_i = \nabla_\xi \partial\Phi/\partial x_i$ and the operator $K$ has the form

$$K_{ij} = \sum_l L_{il} \left.\frac{\partial^2\Phi}{\partial x_l \partial x_j}\right|_{x^{\mathrm{eq}}} \Delta_\xi, \quad i.e. \ \ K = L(D^2\Phi)_{x^{\mathrm{eq}}}\Delta_\xi,$$

where $\Delta_\xi$ is the Laplace operator. This operator $K$ is self-adjoint in the inner product which is just the integral in space of (3). The generalizations to inhomogeneous equilibria, non-isotropic and non-Euclidian spaces are also routine but lead to more cumbersome formulas.

Symmetric operators have many important properties. Their spectrum is real, for a function of a real variable $f$ with real values it is possible to define $f(K)$ through the spectral decomposition of $K$, and this $f(K)$ is also symmetric in the same inner product. This property is the cornerstone for further consideration.

**Symmetry between observables and initial data.** – The exponential of a symmetric operator is also symmetric, hence, Onsager's relations (2) immediately imply

$$\langle a \,|\, \exp(Kt)\, b \rangle \equiv \langle b \,|\, \exp(Kt)\, a \rangle. \tag{4}$$

The expression $x(t) = \exp(Kt)\, b$ gives a solution to the kinetic equations (1) with initial conditions $x(0) = b$. The expression $\langle a \,|\, x(t) \rangle$ is the result of a measurement: formally, for each vector $a$ we can introduce a "device" (an observer), which measures the scalar product of vector $a$ on a current state $x$.

The left-hand side of (4) represents the result of such an experiment: we prepare an initial state $x(0) = b$, start the process from this state and measure $\langle a \,|\, x(t) \rangle$. In the right-hand side, the initial condition $b$ and the observer $a$ exchange their positions and roles: we start from the initial condition $x(0) = a$ and measure $\langle b \,|\, x(t) \rangle$. The result is the same function of time $t$.

This exchange of the observer and the initial state transforms an ideal experiment into another ideal experiment (we call them *dual experiments*). The left- and the right-hand sides of (4) represent different experimental situations but with the same results of the measurements.

This observation produces many consequences. As a first class of examples, we present the time-reversible Markov chains [15], or the same class of kinetic equations, the monomolecular reactions with detailed balance (see any detailed textbook in chemical kinetics, for example, [12]).

Here a terminological comment is necessary. The term "reversible" has three different senses in thermodynamics and kinetics.

- First of all, processes with entropy growth are *irreversible*. In this sense, all processes under consideration are irreversible.

- Secondly, processes with microreversibility, which satisfy the detailed balance and Onsager relations, are *time-reversible* (or, for short, one often calls them "reversible"). We always call them time-reversible to avoid confusion.

- In the third sense, reversibility is the existence of inverse processes: if transition $A \to B$ exists then transition $B \to A$ exists too. This condition is significantly weaker than microreversibility.

"Time-reversibility" of irreversible processes sounds paradoxical and requires comments. The most direct interpretation of "time-reversing" is to go back in time: we take a solution to dynamic equations $x(t)$ and check whether $x(-t)$ is also a solution. For the microscopic dynamics (the Newton or Schrödinger equations) we expect that $x(-t)$ is also a solution to the dynamic equations. Non-equilibrium statistical physics combines this idea with the description of macroscopic or mesoscopic kinetics by an ensemble of elementary processes: collisions, reactions or jumps. The microscopic "reversing of time" turns at this level into the "reversing of arrows": reaction $\sum_i \alpha_i A \to \sum_j \beta_j B_j$ transforms into $\sum_j \beta_j B_j \to \sum_i \alpha_i A$ and conversely. The equilibrium ensemble should be invariant with respect to this transformation. This leads us immediately to the concept of *detailed balance*: each process is equilibrated by its reverse process. "Time-reversible kinetic process" stands for "irreversible process with the time–reversible underlying microdynamics".

We consider a general network of linear reactions. This network is represented as a directed graph (digraph) [12]: vertices correspond to components $A_i$ ($i = 1, 2, \ldots, n$), edges correspond to reactions $A_i \to A_j$ ($i \neq j$). For each vertex, $A_i$, a positive real variable $c_i$ (concentration) is defined. For each reaction, $A_i \to A_j$ a non-negative continuous bounded function, the reaction rate constant $k_{ji} > 0$ is given. The kinetic equations have the standard Master equation form

$$\frac{\mathrm{d}c_i}{\mathrm{d}t} = \sum_{j,\, j \neq i} (k_{ij}c_j - k_{ji}c_i). \tag{5}$$

The principle of detailed balance ("time-reversibility") means that there exists such a positive vector $c_i^{\text{eq}} > 0$ that for all $i, j$ ($j \neq i$)

$$k_{ij} c_j^{\text{eq}} = k_{ji} c_i^{\text{eq}}. \tag{6}$$

The following conditions are necessary and sufficient for existence of such an equilibrium $c_i^{\text{eq}} > 0$:

– Reversibility (in the third sense): if $k_{ji} > 0$ then $k_{ij} > 0$.

– For any cycle $A_{i_1} \to A_{i_2} \to \cdots \to A_{i_q} \to A_{i_1}$ the product of constants of reactions is equal to the product of constants of reverse reactions,

$$\prod_{j=1}^{q} k_{i_{j+1} i_j} = \prod_{j=1}^{q} k_{i_j i_{j+1}}, \tag{7}$$

where $i_{q+1} = i_1$. This is the *Wegscheider identity* [5].

It is sufficient to consider in conditions (7) a finite number of basic cycles [12].

The free entropy function for the Master equation (5) is the (minus) relative entropy

$$Y = -\sum_i c_i \ln\left(\frac{c_i}{c_i^{\text{eq}}}\right). \tag{8}$$

In this form, the function $-RTY$ was used already by L. Onsager [1] under the name "free energy". The entropic inner product for the free entropy (8) is

$$\langle a \mid b \rangle = \sum_i \frac{a_i b_i}{c_i^{\text{eq}}}. \tag{9}$$

Let $c^a(t)$ be a solution of kinetic equations (5) with initial conditions $c^a(0) = a$. Then the reciprocity relations (4) for linear systems with detailed balance take the form

$$\sum_i \frac{b_i c_i^a(t)}{c_i^{\text{eq}}} = \sum_i \frac{a_i c_i^b(t)}{c_i^{\text{eq}}}. \tag{10}$$

Let us use for $a$ and $b$ the vectors of the standard basis in $\mathbb{R}^n$: $a_i = \delta_{iq}$, $b_i = \delta_{ir}$, $q \neq r$. This choice results in the useful particular form of (10). We compare two experimental situations, $c_i^a(0) = \delta_{iq}$ (the process starts at the state "everything is in $A_q$") and $c_i^b(0) = \delta_{ir}$ (the process starts at the state "everything is in $A_r$"); for the first situation we measure $c_r^a(t)$ ("how much $A_r$ is produced from the initial $A_q$"), for the second one we measure $c_q^b(t)$ ("how much $A_q$ is produced from the initial $A_r$"). The reciprocal relations (10) give

$$\frac{c_r^a(t)}{c_r^{\text{eq}}} = \frac{c_q^b(t)}{c_q^{\text{eq}}}. \tag{11}$$

More examples of such relations for chemical kinetics are presented in [16]. It is much more straightforward to check experimentally these relations between kinetic curves than the initial Onsager relations between kinetic coefficients. We give an example of such an experiment below. For processes distributed in space, instead of concentrations of $A$ and $B$ some of their Fourier or wavelet coefficients appear.

**Weak form of detailed balance.** – For many real systems some of the elementary reactions are practically irreversible. Hence the first condition of detailed balance, the reversibility (if $k_{ji} > 0$ then $k_{ij} > 0$) may be violated. Nevertheless, these systems may be considered as *limits* of systems with detailed balance when some of the constants tend to zero. For such limits, the condition (7) persists, and for any cycle the product of constants of direct reactions is equal to the product of constants of reverse reactions.

This is a *weak form of detailed balance* without the obligatory existence of a positive equilibrium. In this section, we consider the systems, which satisfy this weak condition, the *weakly time-reversible* systems.

For a linear system, the following condition is necessary and sufficient for its weak time-reversibility: *in any cycle $A_{i_1} \to A_{i_2} \to \cdots \to A_{i_q} \to A_{i_1}$ with strictly positive constants $k_{i_{j+1} i_j} > 0$ (here $i_{q+1} = i_1$) all the reactions are reversible ($k_{i_j i_{j+1}} 0$) and the identity (7) holds.*

The components $A_q$ and $A_r$ ($q \neq r$) are *strongly connected* if there exist oriented paths both from $A_q$ to $A_r$ and from $A_r$ to $A_q$ (each oriented edge corresponds to a reaction with nonzero reaction rate constant). It is convenient to consider an empty path from $A_i$ to itself as an oriented path.

*For strongly connected components of a weakly time-reversible system, all reactions in any directed path between them are reversible.* This is a structural condition of the weak time-reversibility.

Under this structural condition, the classes of strongly connected components form a partition of the set of components: these classes either coincide or do not intersect and each component belongs to one of them. Each cycle belongs to one class.

Let $A_q$ and $A_r$ be strongly connected. Let us select an arbitrary oriented path $p$ between $A_q$ and $A_r$: $A_q \leftrightarrow A_{i_1} \leftrightarrow A_{i_2} \leftrightarrow \cdots \leftrightarrow A_{i_l} \leftrightarrow A_r$. For the product of direct reaction rate constants in this path we use $K_p^+$ and for the product of reverse reaction rate constants we use $K_p^-$. *The ratio $K_{rq} = K_p^+ / K_p^-$ does not depend on the path $p$ and characterizes the pair $A_r$, $A_q$*, because of the Wegscheider identity (7). This is the quantitative criterion of the weak time-reversibility.

The constant $K_{rq}$ is an analogue to the equilibrium constant. Indeed, for the systems with positive equilibrium and detailed balance, $K_{rq} c_q^{\text{eq}} = c_r^{\text{eq}}$ and $K_{rq} = c_r^{\text{eq}} / c_q^{\text{eq}}$.
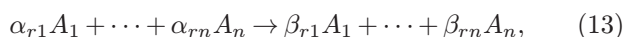
For weakly time-reversible system, the reciprocal relations between kinetic curves can be formulated for any strongly connected pair $A_q$ and $A_r$. Exactly for the same

pair of kinetic curves, as in (11), we obtain

$$\frac{c_r^a(t)}{c_q^b(t)} = K_{rq}. \tag{12}$$

This formula describes two experiments: i) we start the system at $t = 0$ from the pure $A_q$ and measure $c_r(t)$, then ii) we start at $t = 0$ from the pure $A_r$ and measure $c_q(t)$. The ratio of these two kinetic curves, $c_r(t)/c_q(t)$ does not depend on $t$ and is equal to the generalized equilibrium constant $K_{rq}$.

The weak form of the Wegscheider identity for general (nonlinear) kinetic systems is also possible. Let us consider the reaction system:

$$\alpha_{r1}A_1 + \cdots + \alpha_{rn}A_n \to \beta_{r1}A_1 + \cdots + \beta_{rn}A_n, \tag{13}$$

which satisfies the mass action law: $\dot{c} = \sum_r \gamma_r k_r \prod_i c_i^{\alpha_i}$, where $k_r > 0$, $\gamma_{ri} = \beta_{ri} - \alpha_{ri}$ is the stoichiometric vector of the $r$-th reaction, and the reverse reactions with positive constants are included in the list (13) separately.

Let us consider linear relations between vectors $\{\gamma_r\}$:

$$\sum_r \lambda_r \gamma_r = 0 \text{ and } \lambda_r \neq 0 \text{ for some } r. \tag{14}$$

If all the reactions are reversible then the principle of detailed balance gives us the identity [12]:

$$\prod_r (k_r^+)^{\lambda_r} = \prod_r (k_r^-)^{\lambda_r} \tag{15}$$

for any linear relation (14). For reversible reactions, we can take $\lambda_r \geqslant 0$ in (15) for all $r$: if we substitute the reactions with $\lambda_r < 0$ by their reverse reactions, then $\gamma_r$ and $\lambda_r$ change signs. It is sufficient to consider only the cone $\Lambda_+$ of non-negative relations (14) ($\lambda_r \geqslant 0$) and take in (15) the direction vectors of its extreme rays. Let $k_r^- = 0$ for some $r$. The weak form of the identity (15) is

*For any extreme ray of $\Lambda_+$ with a direction vector $\lambda_r \geqslant 0$ the reactions which correspond to the positive coefficients $\lambda_r > 0$ are reversible ($k_r^- > 0$) and their constants satisfy the identity (15).*

**Nonlinear examples.** – It seems impossible to find a general relation between kinetic curves for general nonlinear kinetics far from equilibrium. Nevertheless, simple examples encourage us to look for a non-trivial theory for some classes of nonlinear systems. In this section, we give two examples of nonlinear elementary reactions which demonstrate the equilibrium relations between non-equilibrium kinetic curves [16].

$2A \leftrightarrow B$. The linear conservation law is $c_A + 2c_B = $ const. Let us take two initial states with the same value $c_A + 2c_B = 1$: (a) $c_A(0) = 1$, $c_B(0) = 0$ and (b) $c_A(0) = 0$, $c_B(0) = 1/2$. We will mark the corresponding solutions by the upper indexes $a$, $b$. The mass action law gives

$$\dot{c}_A = -2k^+ c_A^2 + k^-(1 - c_A), \quad c_B = (1 - c_A)/2. \tag{16}$$

The analytic solution easily gives

$$\frac{c_B^a(t)}{c_A^a(t)c_A^a(t)} = \frac{k^+}{k^-} = K^{\text{eq}} = \frac{c_B^{\text{eq}}}{(c_A^{\text{eq}})^2}, \tag{17}$$

the denominator involves the $A$ concentrations of both trajectories, $c^a$ (started from $c_A(0) = 1$, $c_B(0) = 0$) and $c^b$ (started from $c_A(0) = 0$, $c_B(0) = 1/2$). A ratio is equal to the equilibrium constant at every time $t > 0$. This identity between the non-stationary kinetic curves reproduces the equilibrium ratio.

$2A \leftrightarrow 2B$. The linear conservation law is $c_A + c_B = $ const. Let us take two initial states with the same value $c_A + c_B = 1$: a) $c_A(0) = 1$, $c_B(0) = 0$ and b) $c_A(0) = 0$, $c_B(0) = 1$. The kinetic equation is

$$\dot{c}_A = -2k^+ c_A^2 + k^-(1 - c_A)^2, \quad c_B = 1 - c_A. \tag{18}$$

It can be solved analytically. For this solution,

$$\frac{c_B^a(t)c_B^b(t)}{c_A^a(t)c_A^b(t)} = \frac{k^+}{k^-} = K^{\text{eq}} = \frac{(c_B^{\text{eq}})^2}{(c_A^{\text{eq}})^2}, \tag{19}$$

both the numerator and denominator include trajectories for both initial states, $a$ and $b$. This identity between the kinetic curves also reproduces the equilibrium ratio.

**Experimental evidences.** – In this work, we investigate the validity of the reciprocal relations using the TAP (Temporal Analysis of Products) technique proposed by Gleaves in 1988 [17]. It has been successfully applied in many areas of chemical kinetics and engineering for non–steady-state kinetic characterization [18]. The studied reaction is a part of the reversible water gas shift reaction over iron oxide catalyst. The overall reaction is $H_2O + CO \leftrightarrow H_2 + CO_2$.

*Experimental set-up.* The TAP reactor system used in this work is made of quartz and is of the size $33\,\text{mm}$ bed-length and $4.75\,\text{mm}$ inner diameter. The products and the unreacted reactants coming out of the reactor are monitored by a UTI 100 C quadrupole mass spectrometer (QMS). The number of molecules admitted during pulse experiments amounts to $10^{15}$ molecules/pulse.

To ensure uniformity of the catalyst along the bed, we use a thin-zone TAP reactor (TZTR), the width of the catalyst zone being $2\,\text{mm}$. Experiments were performed over $40\,\text{mg}$ of $Fe_2O_3$ catalyst. The catalyst was packed in between two inert zones of quartz particles of the same size ($250 < d_p < 500\,\mu\text{m}$). The temperature of the reactor was measured by a thermocouple positioned in the center of the catalyst bed. Several single-pulse experiments were performed by pulsing CO or $CO_2$ at the temperature of $780\,\text{K}$. In all the experiments, the reaction mixture was prepared with Ar as one of the components, so that the inlet amount of the components can be determined from the Ar response.

*Application to the measurements.* In a thin-zone TAP reactor, the diffusion occurring in the inert zones flanking
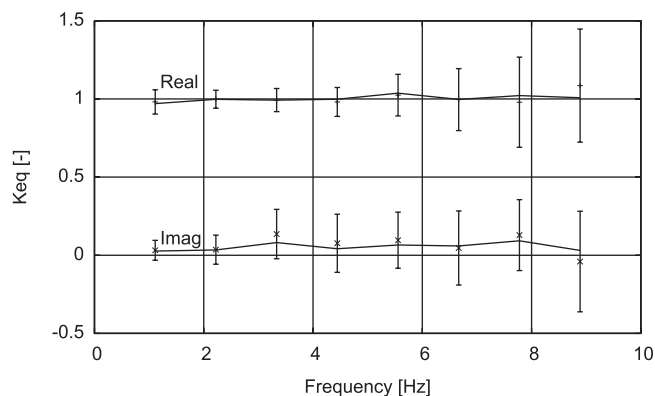
Fig. 1: Fourier domain result values for the "$B$ from $A/A$ from $B$" ratio (20), *vs.* frequency $f$ in Hz (so that $\omega = 2\pi f$, $s = i\omega$); real and imaginary part. The error bars were obtained from 10000 resampled measurements.

the thin reactive zone must be accounted for. The Knudsen regime in these zones guarantees a linear behaviour, so that the resulting outlet fluxes can be expressed in terms of convolutions. Switching to the Laplace domain greatly facilitates the analysis, and we can prove in general that the fixed proportion property is equivalent to the following equality in terms of the exit fluxes $F_{B_A}$ of gas $B$ given a unit inlet pulse of gas $A$ and $F_{A_B}$, of $A$ given a unit inlet pulse of $B$, see [19]:

$$K_{eq} = \frac{(\cosh \sqrt{s\tau_{1,A}})(\sqrt{\tau_{3,B}} \sinh \sqrt{s\tau_{3,B}})}{(\cosh \sqrt{s\tau_{1,B}})(\sqrt{\tau_{3,A}} \sinh \sqrt{s\tau_{3,A}})} \frac{\mathcal{L}F_{B_A}(s)}{\mathcal{L}F_{A_B}(s)} \quad (20)$$

identically in the Laplace variable $s$, where $\tau_{i,G} = \epsilon_i L_i^2/D_G$, $\epsilon_i$ denoting the packing density of the $i$-th zone, $L_i$ its length, and $D_G$ the diffusivity of gas $G$. To apply this in practice, we set $s = i\omega$ and switch to the Fourier domain.

Performing these corrections, with $A$ denoting CO and $B$ $CO_2$, the results of fig. 1 in the Fourier domain are obtained. The real and imaginary parts of the right-hand side in (20) are graphed, with error bars corresponding to three times the standard deviation estimated from resampling 10000 times the exit flux measurements using their principal error components. Ideally, all imaginary values should be zero; we see that zero does lie within all the confidence intervals. We also see that the smallest error in the real parts occurs for the second frequency, $2.2$ Hz. This confidence interval lies snugly within the others, offering confirmation that (within experimental error) the same value for all frequencies is obtained.

**Conclusion.** – The shift in time operator is symmetric in the entropic inner product. Its symmetry allows us to formulate the symmetry relations between the observables and initial data. These relations could be validated without differentiation of empiric curves and are, in that sense, more robust and closer to the direct measurements. For

the Markov processes and chemical kinetics, the symmetry relations between the observables and initial data have an elegant form of the symmetry between "$A$ produced from $B$" and "$B$ produced from $A$": their ratio is equal to the equilibrium constant and does not change in time (11), (12). For processes distributed in space, instead of concentrations of $A$ and $B$ some of their Fourier or wavelet coefficients appear.

The symmetry relations between the observables and initial data have a rich variety of realizations, which makes the direct experimental verification possible. On the other hand, this symmetry provides the possibility to extract information about the experimental data through the dual experiments. These relations are applicable to all systems with microreversibility.

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