

# Equilibrium relationships for non-equilibrium chemical dependencies

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## Abstract

In contrast to common opinion, it is shown that equilibrium constants determine the time-dependent behavior of particular ratios of concentrations for any system of reversible first-order reactions. Indeed, some special ratios actually coincide with the equilibrium constant at any moment in time. This is established for batch reactors, and similar relations hold for steady-state plug-flow reactors, replacing astronomic time by residence time. Such relationships can be termed time invariants of chemical kinetics.

*Key words:* kinetics; transient response; thermodynamics process; batch

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## 1 Introduction

In presenting the foundations of physical chemistry, the basic difference between equilibrium chemical thermodynamics and chemical kinetics is always stressed.

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A typical problem of equilibrium chemical thermodynamics (ECT) is calculating the composition of a chemical mixture that reacts in a closed system for an infinitely long time. ECT does not consider time.

In opposite, chemical kinetics is the science of the evolution of chemical composition in time.

Some selected results of theoretical chemical kinetics are obtained from thermodynamic principles, especially the principle of detailed equilibrium:

- (a) the uniqueness and stability of the equilibrium in any closed system, see (Zeldovich, 1938) and the analysis in (Yablonsky et al., 1991);
- (b) the absence of damped oscillations near the point of detailed equilibrium, see (Wei and Prater, 1962) and the analysis in (Yablonsky et al., 1991);
- (c) some limitations on the kinetic relaxation from the given initial conditions, e.g., based on the known set of equilibrium constants that determine the equilibrium composition, one can find a forbidden domain of compositions that is impossible to reach from the given boundary conditions. See (Gorban et al., 1982; Gorban, 1984; Gorban, Kaganovich et al., 2006).

However, the present dogma of physical chemistry holds that it is impossible to present an expression for any non-steady state chemical system based on its description under equilibrium conditions, except for some relations describing the behavior in the linear vicinity of equilibrium.

The goal of this short note is to announce that, contrary to this ‘dogma’, we have obtained relations of equilibrium type for some non-steady state chemical systems. This has been achieved for all linear cases (with a general proof) and some non-linear ones. In a forthcoming extended paper these relationships will be explained in more detail.

Based on our results, equilibrium thermodynamic relationships can be considered not only as a description of the final point of temporal evolution, but as inherent characteristics of the dynamic picture.

The following are examples to illustrate our statement; in all of them we analyze traditional models of chemical kinetics based on the mass-action law. The processes described by these models occur in a closed non-steady-state chemical system with perfect mixing (batch reactor) or in an open steady-state chemical system with no radial gradient (plug-flow reactor), whose description is identical to the batch reactor, replacing astronomic time by residence time.

In this short communication, we shall analyze a combination of data of different thought experiments, e.g.

- a chemical reactor is primed with a substance  $A$  only,

- it is primed with substance  $B$  only.

In both cases, we shall monitor both concentrations  $A$  and  $B$  and pay special attention to the dependencies of “ $B$  produced from  $A$ ” and “ $A$  produced from  $B$ ”. We shall use the notation  $A_A(t)$  for the temporal concentration dependence of substance  $A$ , given the initial condition  $(A, B, \dots) = (1, 0, \dots)$ , i.e., only  $A$  occurs, with normalized concentration 1. Similarly,  $B_A(t)$  is the concentration of substance  $B$  for the same initial condition;  $A_B(t)$  that of  $A$  when at  $t = 0$ ,  $(A, B, \dots) = (0, 1, \dots)$ . We found interesting relationships between these dependencies.

## 2 Linear cases

2.1 *A single, first-order reversible reaction*  $A \xrightleftharpoons[k_1^-]{k_1^+} B$

By elementary mathematical techniques, for  $t \geq 0$ ,

$$\begin{aligned} A_A(t) &= \frac{k_1^- + k_1^+ \exp(-(k_1^+ + k_1^-)t)}{k_1^+ + k_1^-}, \\ B_A(t) &= \frac{k_1^+ (1 - \exp(-(k_1^+ + k_1^-)t))}{k_1^+ + k_1^-}, \\ A_B(t) &= \frac{k_1^- (1 - \exp(-(k_1^+ + k_1^-)t))}{k_1^+ + k_1^-}, \\ B_B(t) &= \frac{k_1^+ + k_1^- \exp(-(k_1^+ + k_1^-)t)}{k_1^+ + k_1^-}. \end{aligned}$$

Comparing  $B_A$  and  $A_B$ , it is clear that they are constantly in a fixed proportion:

$$\frac{B_A(t)}{A_B(t)} = \frac{k_1^+}{k_1^-} = K_{\text{eq}}, \quad (1)$$

which is the thermodynamic constant of equilibrium. It is remarkable that this ratio holds at any moment of time  $t > 0$ , and not merely in the limit  $t \rightarrow +\infty$ .

2.2 Two consecutive first-order reactions, the first being reversible:  $A \xrightleftharpoons[k_1^-]{k_1^+} B \xrightarrow{k_2^+} C$

Using, e.g., Laplace domain techniques, the following analytical solutions are obtained: if we define the expressions

$$\lambda_{1,2} = \frac{k_1^+ + k_1^- + k_2^+ \pm \sqrt{(k_1^+ + k_1^- + k_2^+)^2 - 4k_1^+k_2^+}}{2} \quad (2)$$

and verify that

$$\lambda_1 > k_2^+ > \lambda_2 > 0, \quad \lambda_1 > k_1^+ > \lambda_2 > 0, \quad (3)$$

we can write

$$\begin{aligned} A_A(t) &= \frac{1}{k_2^+(\lambda_1 - \lambda_2)} \left( \lambda_1(k_2^+ - \lambda_2) \exp(-\lambda_2 t) + \lambda_2(\lambda_1 - k_2^+) \exp(-\lambda_1 t) \right), \\ B_A(t) &= \frac{k_1^+}{\lambda_1 - \lambda_2} (\exp(-\lambda_2 t) - \exp(-\lambda_1 t)), \\ C_A(t) &= 1 - \frac{1}{\lambda_1 - \lambda_2} (\lambda_1 \exp(-\lambda_2 t) - \lambda_2 \exp(-\lambda_1 t)), \\ A_B(t) &= \frac{k_1^-}{\lambda_1 - \lambda_2} (\exp(-\lambda_2 t) - \exp(-\lambda_1 t)), \\ B_B(t) &= \frac{1}{k_2^+(\lambda_1 - \lambda_2)} \left( \lambda_2(\lambda_1 - k_2^+) \exp(-\lambda_2 t) + \lambda_1(k_2^+ - \lambda_2) \exp(-\lambda_1 t) \right), \\ C_B(t) &= 1 - \frac{1}{\lambda_1 - \lambda_2} \left( (\lambda_1 - k_2^+) \exp(-\lambda_2 t) + (k_2^+ - \lambda_2) \exp(-\lambda_1 t) \right). \end{aligned}$$

Again, it turns out that  $B_A$  and  $A_B$  are always in fixed proportion:

$$\frac{B_A(t)}{A_B(t)} = \frac{k_1^+}{k_1^-} = K_{\text{eq}}, \quad (4)$$

and again this is the constant of equilibrium of the  $A \leftrightarrow B$  reaction.

2.3 The cycle of three reversible first-order reactions  $A \xrightleftharpoons[k_1^-]{k_1^+} B \xrightleftharpoons[k_2^-]{k_2^+} C \xrightleftharpoons[k_3^-]{k_3^+} A$

In the Laplace domain, defining the symbols

$$\begin{aligned}
\sigma_1 &= k_1^+ + k_1^- + k_2^+ + k_2^- + k_3^+ + k_3^- \\
\sigma_2 &= k_1^+ k_2^+ + k_2^+ k_3^+ + k_3^+ k_1^+ + k_1^- k_2^- + k_2^- k_3^- + k_3^- k_1^- + \\
&\quad k_1^- k_3^- + k_2^- k_1^- + k_3^- k_2^- \\
\Delta(s) &= s(s^2 + \sigma_1 s + \sigma_2),
\end{aligned}$$

the transformed concentrations  $A_A$ ,  $B_A$  and  $A_B$  are given by

$$\begin{aligned}
\mathcal{L}A_A(s) &= \frac{s^2 + (k_1^- + k_3^+ + k_2^+ + k_2^-)s + (k_1^- k_3^+ + k_1^- k_2^- + k_2^+ k_3^+)}{\Delta(s)} \\
\mathcal{L}B_A(s) &= \frac{k_1^+ s + (k_1^+ k_3^+ + k_1^+ k_2^- + k_2^- k_3^-)}{\Delta(s)} \\
\mathcal{L}A_B(s) &= \frac{k_1^- s + (k_1^- k_3^+ + k_1^- k_2^- + k_2^+ k_3^+)}{\Delta(s)}
\end{aligned}$$

and the ratio of the latter two, by

$$\begin{aligned}
\frac{\mathcal{L}B_A(s)}{\mathcal{L}A_B(s)} &= \frac{k_1^+ s + (k_1^+ k_3^+ + k_1^+ k_2^- + k_2^- k_3^-)}{k_1^- s + (k_1^- k_3^+ + k_1^- k_2^- + k_2^+ k_3^+)} \\
&= \frac{k_1^+}{k_1^-} \left( 1 - \frac{1}{1 + k_1^- \frac{k_1^+ k_3^+ + k_1^+ k_2^- + k_2^- k_3^- + s k_1^+}{k_1^+ k_2^+ k_3^+ - k_1^- k_2^- k_3^-}} \right) \\
&= \frac{k_1^+}{k_1^-},
\end{aligned}$$

where the Onsager relationship  $k_1^+ k_2^+ k_3^+ = k_1^- k_2^- k_3^-$  was used in the final step. Hence for all  $s$ ,  $\mathcal{L}B_A(s)$  and  $\mathcal{L}A_B(s)$  are in fixed proportion given by the equilibrium constant ( $k_1^+/k_1^-$ ). Since the inverse Laplace transform is linear, the same proportion holds in the time domain:

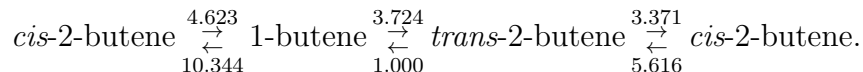
$$\frac{B_A(t)}{A_B(t)} = \frac{k_1^+}{k_1^-} = K_{\text{eq},1}, \quad (5)$$

Similarly,

$$\frac{C_B(t)}{B_C(t)} = \frac{k_2^+}{k_2^-} = K_{\text{eq},2}, \quad \frac{A_C(t)}{C_A(t)} = \frac{k_3^+}{k_3^-} = K_{\text{eq},3}, \quad (6)$$

As an example, we show in Fig. 1 the time dependence of  $B_A/A_A$ ,  $B_B/A_B$  and the time-invariant ratio  $B_A/A_B$ , for the case of isomerization of butenes

in (Wei and Prater, 1962), eq. (129):



This behavior is typical of the examples given here: if the system is started from the initial values  $(A, B, C) = (1, 0, 0)$ , the ratio  $B_A/A_A$  grows at first from 0, eventually reaching the equilibrium value (note that for these parameters  $B_A/A_A$  slightly overshoots the limit). Similarly, when started from  $(0, 1, 0)$ , the corresponding  $B_B/A_B$  initially decreases from  $+\infty$  and eventually reaches same limit, viz the equilibrium ratio. But surprisingly the combination  $B_A/A_B$  is constantly equal to the equilibrium value, for all times  $t > 0$ .



Although the expressions become more involved, it is straightforward to verify that in this case the fixed equilibrium proportions also hold, given the Onsager relationship  $k_1^+ k_2^+ k_3^+ k_4^+ = k_1^- k_2^- k_3^- k_4^-$ :

$$\frac{B_A(t)}{A_B(t)} = \frac{k_1^+}{k_1^-} = K_{\text{eq},1}, \quad (7)$$

and similarly for  $C_B/B_C$ ,  $D_C/C_D$  and  $A_D/D_A$ . Furthermore

$$\frac{C_A(t)}{A_C(t)} = \frac{k_1^+ k_2^+}{k_1^- k_2^-} = K_{\text{eq},1} K_{\text{eq},2}, \quad (8)$$

with a similar relationship for  $D_B/B_D$ .

## 2.5 *Sketch of proof for general systems of first-order reactions*

We use the terminology and results of (Roelant et al., 2010). Let  $A$  and  $B$  be substances such that a path from either to the other exists. In view of Onsager relations, then there must exist a reversible path from  $A$  to  $B$ . The denominators of  $A_B$  and  $B_A$  in the Laplace domain are the same, but their numerators differ. For  $A_B$ , the numerator consists of contributions from all forests where  $A$  is the root of a tree and  $B$  is in that tree. Let  $Z, X, Y$  denote

other nodes as in the denominator of the left-hand term in (9):

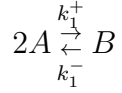
$$\frac{Z \rightarrow A \rightarrow X \rightarrow B \leftarrow Y}{Z \rightarrow A \leftarrow X \leftarrow B \leftarrow Y} = \frac{k_{A \rightarrow X} k_{X \rightarrow B}}{k_{X \rightarrow A} k_{B \rightarrow X}} = K_{A \rightarrow \dots \rightarrow B} \quad (9)$$

Reversing the  $X \rightarrow A$  and  $B \rightarrow X$  arrows amounts to multiplying the forest's term by  $(k_{A \rightarrow X} k_{X \rightarrow B}) / (k_{X \rightarrow A} k_{B \rightarrow X})$ . In view of the Onsager relations, this value does not depend on  $X$ , but only on  $A$  and  $B$ ; in fact, it is the equilibrium constant  $K_{A \rightarrow \dots \rightarrow B}$ . If several  $X$  or  $Y$  or  $Z$  occur, the reasoning is the same. Consequently, every term in the numerator of  $A_B$  is in that proportion to the corresponding term in the numerator of  $B_A$ , and the fixed proportion for all  $s$  translates directly to the time domain:

$$\frac{B_A(t)}{A_B(t)} = K_{A \rightarrow \dots \rightarrow B}. \quad (10)$$

### 3 Nonlinear cases

#### 3.1 Nonlinear reversible reaction (forward second order, backward first order)



In accordance to the mass conservation law, the balance is

$$A(t) + 2B(t) = 1$$

In order for the  $A$  and  $B$  trajectories to reach the same equilibrium, we choose to start them from  $(1, 0)$  and  $(0, 1/2)$  respectively. The nonlinear differential equation is

$$\frac{dA(t)}{dt} = -2k_1^+ A^2(t) + k_1^-(1 - A(t))$$

which can be solved analytically as

$$A_A(t) = \frac{\sqrt{8 \frac{k_1^+}{k_1^-} + 1} + \tanh\left(\frac{1}{2} t k_1^+ \sqrt{8 \frac{k_1^+}{k_1^-} + 1}\right)}{\sqrt{8 \frac{k_1^+}{k_1^-} + 1} + \left(4 \frac{k_1^+}{k_1^-} + 1\right) \tanh\left(\frac{1}{2} t k_1^+ \sqrt{8 \frac{k_1^+}{k_1^-} + 1}\right)}$$

$$B_A(t) = \frac{2 \frac{k_1^+}{k_1^-} \tanh \left( \frac{1}{2} t k_1^+ \sqrt{8 \frac{k_1^+}{k_1^-} + 1} \right)}{\sqrt{8 \frac{k_1^+}{k_1^-} + 1 + \left( 4 \frac{k_1^+}{k_1^-} + 1 \right) \tanh \left( \frac{1}{2} t k_1^+ \sqrt{8 \frac{k_1^+}{k_1^-} + 1} \right)}}$$

$$A_B(t) = \frac{2 \tanh \left( \frac{1}{2} t k_1^+ \sqrt{8 \frac{k_1^+}{k_1^-} + 1} \right)}{\sqrt{8 \frac{k_1^+}{k_1^-} + 1 + \tanh \left( \frac{1}{2} t k_1^+ \sqrt{8 \frac{k_1^+}{k_1^-} + 1} \right)}}$$

The remarkable proportion in this case differs slightly from the linear examples:

$$\frac{B_A}{A_A A_B} = \frac{k_1^+}{k_1^-} = K_{\text{eq},1}$$

we see that the denominator involves the  $A$  concentrations of both trajectories,  $A_A$  and  $A_B$ . Only this can ensure a ratio that equals the equilibrium constant at every time  $t > 0$ .

### 3.2 Nonlinear reversible reaction (forward and backward second order) $2A \xrightleftharpoons[k_1^-]{k_1^+} 2B$

The mass conservation law is

$$A(t) + B(t) = 1,$$

which offers no difficulties for the initial values,  $(1, 0)$  and  $(0, 1)$ . The differential equation

$$\frac{dA(t)}{dt} = -2k_1^+ A^2(t) + 2k_1^- (1 - A(t))^2$$

can be solved analytically as

$$A_A(t) = \frac{1}{1 + \sqrt{\frac{k_1^+}{k_1^-}} \tanh \left( 2t \sqrt{k_1^+ k_1^-} \right)}$$



$$\begin{aligned}
B_A(t) &= \frac{\sqrt{\frac{k_1^+}{k_1^-}} \tanh\left(2t\sqrt{k_1^+k_1^-}\right)}{1 + \sqrt{\frac{k_1^+}{k_1^-}} \tanh\left(2t\sqrt{k_1^+k_1^-}\right)} \\
A_B(t) &= \frac{\sqrt{\frac{k_1^-}{k_1^+}} \tanh\left(2t\sqrt{k_1^+k_1^-}\right)}{1 + \sqrt{\frac{k_1^-}{k_1^+}} \tanh\left(2t\sqrt{k_1^+k_1^-}\right)} \\
B_B(t) &= \frac{1}{1 + \sqrt{\frac{k_1^-}{k_1^+}} \tanh\left(2t\sqrt{k_1^+k_1^-}\right)}.
\end{aligned}$$

Again eliminating time, the similar proportion for this case is

$$\frac{B_A B_B}{A_A A_B} = \frac{k_1^+}{k_1^-} = K_{\text{eq},1},$$

where both numerator and denominator have undergone a duplication in  $A$  and  $B$  trajectories, still producing the equilibrium constant at all times  $t > 0$ .

## 4 Conclusions

We are going to describe these results in detail in a full-length paper. Then the similar approach will be applied to different systems, i.e., CSTR reactors, to reaction-diffusion TAP systems, etc.

Presenting simply the result of this paper, it is a surprising relationship between  $A$  from  $B$  and  $B$  from  $A$ . An “ABBA rule” for short, which reminds the authors of their youth.

*“They speak strangely but I understand” — ABBA, “Eagle” (1978).*

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*Caption to figure*

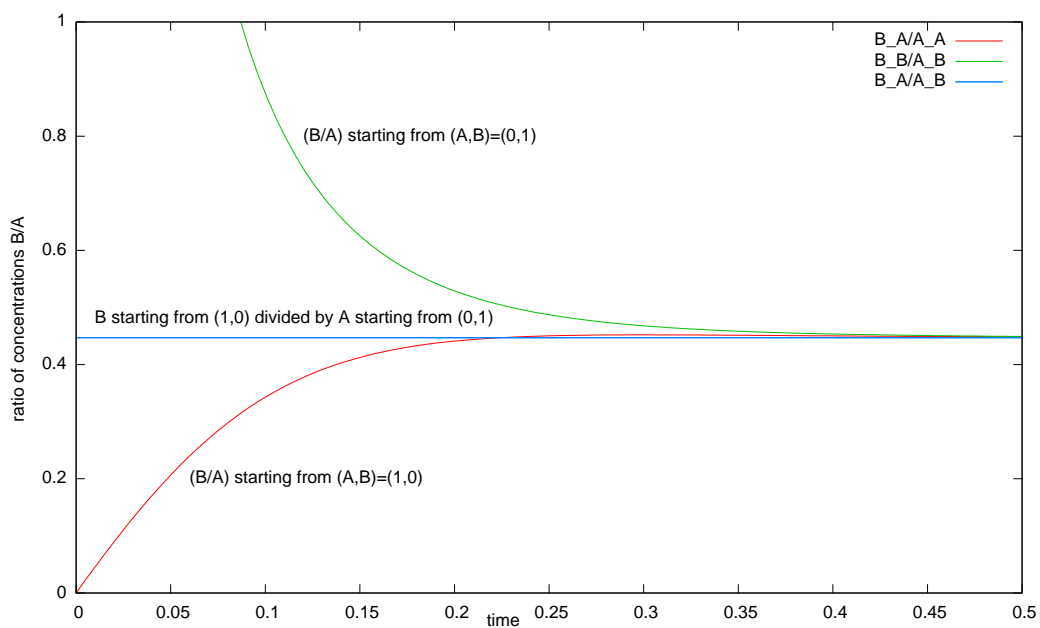


Fig. 1. Time dependence of  $B_A/A_A$ ,  $B_B/A_B$  and the time-invariant ratio  $B_A/A_B$ , for the case of isomerization of butenes in (Wei and Prater, 1962), eq. (129).