



Coincidences in chemical kinetics: Surprising news about simple reactions

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ABSTRACT

New properties of intersections and coincidences of transient concentration curves were discovered and are presented analytically using the classical consecutive mechanism $A \rightarrow B \rightarrow C$ as an example. We identify six different special points, and analyze and classify the six possible (out of 612 combinations) patterns of concentration peak and intersection times and values that distinguish the parameter subdomains and sometimes can eliminate the mechanism. This developed theory is tested on examples (multi-step radioactive decay, isomerization reaction). The mathematical analysis relies on a combination of elementary and symbolic techniques, special functions and numerical approximations.

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Well met, Gentlemen, this is lucky that we meet so just together at this very door. Izaak Walton and Charles Cotton, *The Compleat Angler* (1676).

1. Introduction

Among the innumerable processes which take place in chemistry and chemical engineering, there are some whose features have as yet been woefully neglected. The goal of the present paper is to distinguish and describe one family of such features, i.e., intersection and coincidences of dependencies which exhibit an unexpected elegance, both physical-chemical and mathematical. Most of the results will be obtained analytically, computer calculations will be used only to solve certain transcendental equations and be mentioned as such.

1.1. Consecutive reactions: what was known before

Consecutive reactions are one of the best-known basic mechanisms in chemical kinetics. The simplest example of such

sequential reactions is $A \rightarrow B \rightarrow C$. Many important chemical processes are described via this scheme of reactions. The simplest kinetic model is presented as follows:

$$\frac{dC_A}{dt} = -k_1 C_A, \quad (1)$$

$$\frac{dC_B}{dt} = k_1 C_A - k_2 C_B, \quad (2)$$

$$\frac{dC_C}{dt} = k_2 C_B, \quad (3)$$

where C_A , C_B , C_C are the concentrations of the substances A , B , C , respectively, and k_1 and k_2 (1/s) are the rate constants of the first and second reaction, respectively. The temperature dependency of these rate constants is to be of Arrhenius-type,

$$k_i = k_{i,0} \exp\left(-\frac{E_{A,i}}{RT}\right), \quad (4)$$

where $k_{i,0}$ is a pre-exponential factor (1/s), $E_{A,i}$ the activation energy (kJ/mol), R universal gas constant (kJ/molK), T is absolute temperature (K).

The solution of this simple system equations can be found in many popular textbooks (Hlavacek et al., 2007) 37b, (Froment and Bischoff, 1990), on physical chemistry and chemical kinetics, even on Wikipedia. If $C_{C,0} = 0$, the results are well known:

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when $k_1 \neq k_2$

$$C_A(t) = C_{A,0} \exp(-k_1 t), \quad (5)$$

$$C_B(t) = C_{A,0} k_1 \frac{\exp(-k_1 t) - \exp(-k_2 t)}{k_2 - k_1} + C_{B,0} \exp(-k_2 t), \quad (6)$$

$$C_C(t) = C_{A,0} \left[1 - \frac{k_2 \exp(-k_1 t) - k_1 \exp(-k_2 t)}{k_2 - k_1} \right] + C_{B,0} (1 - \exp(-k_2 t)), \quad (7)$$

so that

$$C_A(t) + C_B(t) + C_C(t) = C_{A,0} + C_{B,0}, \quad t \geq 0. \quad (8)$$

Otherwise, when $k_1 = k_2$ the system has a different type of solution due to the coincidence of both exponential decays. By direct solution or using the Laplace domain (see Appendix C), it is seen that

$$C_A(t) = C_{A,0} \exp(-k_1 t), \quad (9)$$

$$C_B(t) = (C_{A,0} k_1 t + C_{B,0}) \exp(-k_1 t), \quad (10)$$

$$C_C(t) = C_{A,0} [1 - (1 + k_1 t) \exp(-k_1 t)] + C_{B,0} (1 - \exp(-k_1 t)). \quad (11)$$

From here on we assume also $C_{B,0} = 0$. Such formulas can be found e.g. in Eremin (1976) and Bairamov (2003, p. 49), who presented this solution for $C_B(t)$.

Obviously the concentration $C_B(t)$ is characterized by a maximum over time, which is a fingerprint of the consecutive scheme $A \rightarrow B \rightarrow C$ contrary to the parallel scheme $A \rightarrow B, A \rightarrow C$. For the latter mechanism, the kinetic model is presented as follows:

$$\frac{dC_A}{dt} = -(k_1 + k_2)C_A, \quad (12)$$

$$\frac{dC_B}{dt} = k_1 C_A, \quad (13)$$

$$\frac{dC_C}{dt} = k_2 C_A. \quad (14)$$

The solution of Eqs. (12)–(14) is

$$C_A(t) = C_{A,0} \exp(-(k_1 + k_2)t), \quad (15)$$

$$C_B(t) = C_{A,0} \frac{k_1}{k_1 + k_2} [1 - \exp(-(k_1 + k_2)t)], \quad (16)$$

$$C_C(t) = C_{A,0} \frac{k_2}{k_1 + k_2} [1 - \exp(-(k_1 + k_2)t)]. \quad (17)$$

Obviously, in this scheme there is no maximum of any of the concentrations: C_A only decreases, C_B and C_C only increase.

The time of the peak of $C_B(t)$ for the consecutive scheme is also presented in the references: from

$$C'_B(t) = C_{A,0} k_1 \frac{-k_1 \exp(-k_1 t) + k_2 \exp(-k_2 t)}{k_2 - k_1} = 0 \quad (18)$$

one solves

$$t_{B,\max} = \frac{\ln\left(\frac{k_1}{k_2}\right)}{k_1 - k_2}. \quad (19)$$

That this satisfies the physicality requirement $t_{B,\max} > 0$ follows from the elementary considerations outlined in Appendix A. The maximum value of C_B is then given by

$$C_B(t_{B,\max}) = C_{A,0} \left(\frac{k_2}{k_1}\right)^{k_2/(k_1 - k_2)} = C_{A,0} \rho^{\rho/(1-\rho)}, \quad (20)$$

where we introduce the dimensionless ratio of rate constants $\rho = k_2/k_1$. See Fig. 1 for the trend of this peak value as a function of ρ .

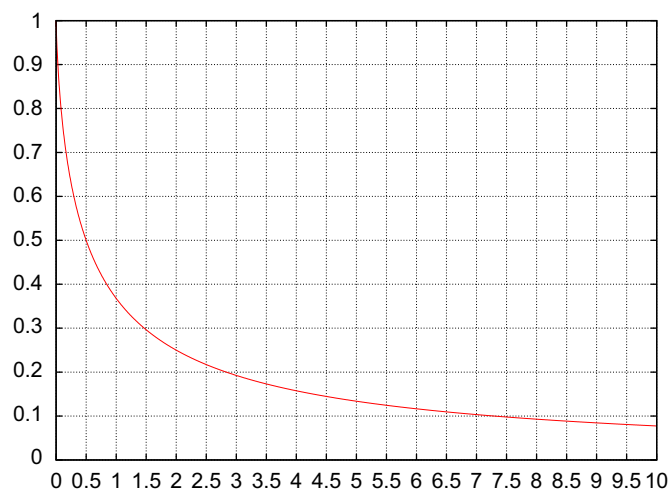


Fig. 1. Plot of $\rho^{\rho/(1-\rho)}$ vs. $0 \leq \rho \leq 10$; this is $C_{B,\max}$ as a function of $\rho = k_2/k_1$.

When $k_1 = k_2$, relying on (9)–(11) and equating the time derivative of $C_B(t)$ to zero, the maximum of $C_B(t)$ occurs at the time

$$t_{B,\max} = \frac{1}{k_1} = \frac{1}{k_2} \quad (21)$$

and there is a remarkable relationship, which is not widely known:

$$C_B(t_{B,\max}) = C_{A,0} e^{-1}. \quad (22)$$

Studying this consecutive mechanism, we found it independently, but later discovered that it was already mentioned in Kubasov (2004). We propose to call this case $k_1 = k_2$ the Euler point E .

To our present knowledge, Eqs. (1)–(22) comprise all theoretical results obtained for this consecutive scheme. Presently we shall reveal and explain some, to our knowledge as yet unknown, properties of this very simple scheme.

2. New results on the maximum of C_B

2.1. Concentration patterns and comparison of rate constants

Calculating the concentration of A at $t_{B,\max}$ from (5) or (9), $C_A(t_{B,\max}) = C_{A,0} \rho^{1/(\rho-1)}$ when $\rho \neq 1$, $C_{A,0} e^{-1}$ otherwise. Consequently,

$$(C_B(t_{B,\max})/C_{A,0}) = (C_A(t_{B,\max})/C_{A,0})^\rho. \quad (23)$$

This is clearly illustrated by the pattern shown on the figures: if $k_1 = k_2$ (as mentioned) the concentrations are equal (Fig. 7); if $k_1 < k_2$ then the concentration of A exceeds that of B (Fig. 9); if $k_1 > k_2$ then the concentration of B exceeds that of A (Fig. 4). Looking at experimental dependencies with these patterns, and assuming the presented consecutive mechanism, we immediately obtain an indication of the comparison between k_1 and k_2 .

2.2. Observability of the Euler point

The question arises whether and if so, when the Euler point is observed, and, more generally, when a given value $\tilde{\rho}$ of k_2/k_1 can be obtained through variation of the temperature T . We assume the Arrhenius dependency of the rate coefficients (4). Solving in these terms $k_2 = \tilde{\rho} k_1$ for T , we find formally that

$$T_{\tilde{\rho}} = \frac{1}{R} \frac{E_{A,1} - E_{A,2}}{\ln(\tilde{\rho} k_{1,0}/k_{2,0})}. \quad (24)$$

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