Teaching and learning materials on the quasi-steady-state approximation and the partial-equilibrium approximation

Agnès Pellissier-Tanon*[1,2], Gabriel Morgado[1], Ludovic Jullien[2], and Annie Lemarchand*[1]

[1]Laboratoire de Physique Théorique de la Matière Condensée, Sorbonne Université, CNRS , 4 place Jussieu, case courrier 121, 75252 Paris CEDEX 05, France
[2]Laboratoire PASTEUR, Département de chimie, École normale supérieure, PSL University, Sorbonne Université, CNRS, 24 rue Lhomond, 75005 Paris, France

Two approximations exploiting evolutions at different time scales are usually used to simplify rate laws in chemical kinetics.[1–5] The quasi-steady-state approximation (QSSA) is used to eliminate a chemical species which evolves faster than the others.[6] The partial-equilibrium approximation (PEA) is employed to remove a reaction step associated with an extent evolving faster than the other extents. Both methods are examples of adiabatic elimination of a fast variable in differential equations.[7–16] The fast variable, concentration or extent, is supposed to instantaneously adapt to the evolution of the other variables. For this reason, the fast variable is sometimes called a slave variable.[17] The fast variable is not independent from the other variables and can be ignored in the reduced rate equations. Quasi-steady state or partial equilibrium does not mean that the eliminated variable has reached a steady state but that it keeps evolving at a rate imposed by the other variables. Far from being stationary, the evolution of the eliminated variable occurs at the time scale on which the reduced rate equations focus.

1 Simple example of quasi-steady-state approximation

The first-order reaction scheme

$$\mathrm{X} \xrightarrow{k_1} \mathrm{Y} \xrightarrow{k_2} \mathrm{Z} \tag{1}$$

is associated with the rate equations

$$\frac{\mathrm{d}X}{\mathrm{d}t} = -k_1 X \tag{2}$$

$$\frac{\mathrm{d}Y}{\mathrm{d}t} = k_1 X - k_2 Y \tag{3}$$

that can be easily solved leading to

$$X(t) = X(0)\exp(-k_1 t) \tag{4}$$

$$Y(t) = \frac{k_1 X(0)}{k_2 - k_1}\exp(-k_1 t) + \left(Y(0) - \frac{k_1 X(0)}{k_2 - k_1}\right)\exp(-k_2 t) \tag{5}$$

If the rate constant k_1 associated with the formation of species Y is much smaller than the rate constant k_2 associated with the consumption of Y, the concentration Y possesses an exponential component $\exp(-k_2 t)$ evolving faster than the concentration X which evolves as $\exp(-k_1 t)$. At a time scale larger than $1/k_2$, the fast exponential component of Y is negligible leading to

$$X(t) = X(0)\exp(-k_1 t) \tag{6}$$

$$Y(t) \simeq \frac{k_1 X(0)}{k_2}\exp(-k_1 t) \tag{7}$$

where $k_2 - k_1 \simeq k_2$ has been used. Equations (6, 7) imply

$$Y(t) \simeq \frac{k_1}{k_2} X(t) \tag{8}$$

which is straightforwardly deduced from Eq. (3) assuming $\frac{\mathrm{d}Y}{\mathrm{d}t} = 0$. Hence, the quasi-steady-state approximation does not impose that Y has reached a steady-state for which $\frac{\mathrm{d}X}{\mathrm{d}t} = 0$ would be also necessary. According to Eq. (8), the approximation imposes that Y follows the evolution of X.

The evolution of the concentration X given in Eq. (6) can be associated with the reduced reaction scheme

$$\mathrm{X} \xrightarrow{k_1} \mathrm{Z} \tag{9}$$

in which the fast variable Y has been eliminated. In this simple example with a reactive intermediate Y, the concentration Y is smaller than X, which does not provide a general validity condition for the elimination of Y using QSSA. The application of the approximation requires a condition on the time scales characterizing the evolution of the concentrations. In this simple example, the condition is $k_1 \ll k_2$.

2 Simple example of partial-equilibrium approximation

The first-order reaction scheme

$$\mathrm{X} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Y} \xrightarrow{k_2} \mathrm{Z} \tag{10}$$

with rate constants obeying $k_1 \gg k_2$ and $k_{-1} \gg k_2$ is associated with the following rate equations for the extents of reaction ξ_1 and ξ_2 associated with the first and second steps

$$\frac{\mathrm{d}\xi_1}{\mathrm{d}t} = k_1 X - k_{-1} Y \tag{11}$$

$$\frac{\mathrm{d}\xi_2}{\mathrm{d}t} = k_2 Y \tag{12}$$

where X and Y are the concentrations of species X and Y. The rate equations for the concentrations are

$$\frac{\mathrm{d}X}{\mathrm{d}t} = -k_1 X + k_{-1} Y \tag{13}$$

$$\frac{\mathrm{d}Y}{\mathrm{d}t} = k_1 X - (k_{-1} + k_2)\, Y \tag{14}$$

$$\frac{\mathrm{d}Z}{\mathrm{d}t} = k_2 Y \tag{15}$$

leading to

$$\frac{\mathrm{d}\xi_1}{\mathrm{d}t} = -\frac{\mathrm{d}X}{\mathrm{d}t} \tag{16}$$

$$\frac{\mathrm{d}\xi_2}{\mathrm{d}t} = \frac{\mathrm{d}Z}{\mathrm{d}t} \tag{17}$$

The law of conservation of matter imposes

$$X + Y + Z = C_{\mathrm{tot}} \tag{18}$$

where C_{tot} is the total concentration. For vanishing extents at the steady state, $(X_0, Y_0, Z_0) = (0, 0, C_{\mathrm{tot}})$, the relationships between the concentrations and the extents are deduced from the integration of Eqs. (16, 17) leading to

$$\xi_1 = -X \tag{19}$$

$$\xi_2 = -X - Y \tag{20}$$

Eqs. (11, 12, 19, 20) are used to write the rate equations for the extents:

$$\frac{\mathrm{d}\xi_1}{\mathrm{d}t} = -\left(k_1 + k_{-1}\right)\xi_1 + k_{-1}\xi_2 \tag{21}$$

$$\frac{\mathrm{d}\xi_2}{\mathrm{d}t} = k_2\xi_1 - k_2\xi_2 \tag{22}$$

that can be solved using standard linear algebra calculations. For $k_1 \gg k_2$ and $k_{-1} \gg k_2$, it reads

$$\xi_1(t) \simeq \frac{k_{-1}}{\sqrt{(k_1+k_{-1})^2 + k_{-1}^2}} A(0) \exp\left(-\frac{k_1 k_2}{k_1+k_{-1}} t\right) - B(0) \exp\left(-\left(k_1+k_{-1}\right) t\right) \tag{23}$$

$$\xi_2(t) \simeq \frac{k_1+k_{-1}}{\sqrt{(k_1+k_{-1})^2 + k_{-1}^2}} A(0) \exp\left(-\frac{k_1 k_2}{k_1+k_{-1}} t\right) + \frac{k_2}{k_1+k_{-1}} B(0) \exp\left(-\left(k_1+k_{-1}\right) t\right) \tag{24}$$

with

$$A(0) = \frac{k_2\sqrt{(k_1+k_{-1})^2 + k_{-1}^2}}{(k_1+k_{-1})^2} \xi_1(0) + \frac{\sqrt{(k_1+k_{-1})^2 + k_{-1}^2}}{k_1+k_{-1}} \xi_2(0) \tag{25}$$

$$B(0) = -\xi_1(0) + \frac{k_{-1}}{k_1+k_{-1}} \xi_2(0) \tag{26}$$

where $\xi_1(0)$ and $\xi_2(0)$ are the initial values of the extents.

The extents are given by weighted sums of two exponential components with two different characteristic times, a short time $1/(k_1+k_{-1})$ and a long time $(k_1+k_{-1})/k_1k_2$. For the extent ξ_1, the prefactor $\frac{k_{-1}}{\sqrt{(k_1+k_{-1})^2+k_{-1}^2}}$ associated with the long characteristic time is smaller than the absolute prefactor equal to 1 associated with the short characteristic time. Over the short time scale $t \leq 1/(k_1+k_{-1})$ the extent ξ_1 evolves as the fast exponential component provided that the initial conditions obey

$$\mid A(0) \mid \leq \mid B(0) \mid \tag{27}$$

The extent ξ_1 is considered as the fast variable.

Over the long time scale $t \gg 1/(k_1+k_{-1})$, the fast exponential decays in Eqs. (23,24) are negligible leading to

$$\xi_1(t) \simeq \frac{k_{-1}}{\sqrt{(k_1+k_{-1})^2 + k_{-1}^2}} A(0) \exp\left(-\frac{k_1 k_2}{k_1+k_{-1}} t\right) \tag{28}$$

$$\xi_2(t) \simeq \frac{k_1+k_{-1}}{\sqrt{(k_1+k_{-1})^2 + k_{-1}^2}} A(0) \exp\left(-\frac{k_1 k_2}{k_1+k_{-1}} t\right) \tag{29}$$

which amounts to

$$\xi_1(t) \simeq \frac{k_{-1}}{k_1+k_{-1}} \xi_2(t) \tag{30}$$

or, according to Eq. (21), to

$$\frac{\mathrm{d}\xi_1}{\mathrm{d}t} = 0 \tag{31}$$

The partial-equilibrium approximation consists in considering that the fast exponential component instantaneously relaxes which amounts to eliminating the fast extent ξ_1. However the fast extent ξ_1 has not reached a steady state but it keeps evolving at the rate imposed by the extent ξ_2. In other words, the reaction associated with the fast extent ξ_1 adapts to the instantaneous value of the other extent ξ_2: The fast extent reaches a pseudo-equilibrium state for each value of the slowly evolving extent as in an adiabatic process.

The elimination of the fast extent ξ_1 leads to the reduced reaction scheme

$$\mathrm{Y} \xrightarrow{\frac{k_1 k_2}{k_1+k_{-1}}} \mathrm{Z} \tag{32}$$

that needs to be supplemented by the relationship

$$X = \frac{k_{-1}}{k_1} Y \tag{33}$$

deduced from Eqs. (11,31).

3 Elimination of a fast variable

The quasi-steady-state approximation (QSSA) and the partial-equilibrium approximation (PEA) offer well-known methods to eliminate a fast variable, a concentration or an extent.[15,18–22]

These approximations are zeroth-order perturbation methods consisting in writing $\frac{\mathrm{d}v_i}{\mathrm{d}t} = 0$ for a fast variable v_i in a system of differential equations involving n variables.[4,5,23–27]

After linearization of the system of differential equations around a stable steady state, standard linear algebra calculations give the expression of each variable in the form of a weighted sum of exponential decays. The weights depend on the rate constants and the initial conditions. In particular, the characteristic times are defined as the inverse of the absolute real part of the eigenvalues of the Jacobian matrix.

The elimination of the fast variable v_i can be performed if two necessary conditions are fulfilled.[5] First, one characteristic time τ_s must be much smaller than the others, leading to a fast exponential decay. Second, the weight of the fast exponential decay $\exp(-t/\tau_s)$ must be larger than or equal to the weight of each other exponential decay in the expression of the variable v_i. These two conditions involve the rate constants. In addition, the approximation is valid for appropriate initial conditions such that the variables have reached the so-called slow manifold of dimension $n-1$[14–16] defined by

$$\frac{\mathrm{d}v_i}{\mathrm{d}t} = 0 \tag{34}$$

over the long time scale obeying $t \gg \tau_s$. On the slow manifold, the variable v_i adapts to the evolution of the other variables and evolves at a rate imposed by them.

After the elimination of the fast variable v_i, the system of differential equations governing the evolution of the other variables can be written as a system of dimension $n-1$. If this system of differential equations for concentrations involves polynomials compatible with chemical kinetics rate laws, the evolution of the remaining chemical species can be associated with a reduced set of reaction steps. The existence of a reduced reaction scheme is not always guaranteed as illustrated by Michaelis-Menten kinetics which leads to rational functions of the concentrations in the rate equations.[21] If the remaining characteristic times have different orders of magnitude, an analogous procedure of elimination may be performed to further reduce the number of variables.

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