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On the validity of the steady-state approximation in non-isothermal kinetics. Part II

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Abstract

The authors discuss the steady-state approximation for variable temperature and, implicitly in time, kinetic constants, within the framework of the kinetic analysis of a sequence of two first-order consecutive reactions with an active intermediate. It is thus demonstrated that the steady-state approximation as used in isothermal kinetics may also be applied in the non-isothermal kinetics.

Keywords: Kinetics; Non-isothermal

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1. Introduction

In a recent note concerning the correctness of the rate expression for non-isothermal kinetics, Nawada argues against the steady-state approximation under such conditions [1]. His argument rests on two major statements, namely:

1. "The constancy of [A*] (where [A*] is the concentration of the activated complex) is inappropriate because this is only an assumption in one of the methods of solving the unimolecular gas-phase reaction taking place under steady-state conditions".
2. The steady-state condition with respect to the activated complex "describes only isothermal processes, it cannot be readily extended to non-isothermal processes with the same zero value for the derivative".

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Concerning statement 1, one has to emphasize that although inadequate, the term "constant" for the concentration of the active intermediate was used by Eyring et al. [2]. As each elementary reaction, regardless of molecularity or order, has its own activated complex (transition state), the steady-state with respect to it as an active intermediate is generally valid, not being limited to unimolecular reactions.

Concerning the possibility to extend the steady-state approximation under non-isothermal conditions (statement 2), some qualitative considerations have been given in a previous note as an answer to Nawada's criticism [3]. In this paper we aim to offer a demonstration regarding the validity of the steady-state approximation.

2. Theory

Let us consider the classical sequence of two first-order consecutive reactions

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \tag{1}$$

k_1 and k_2 being their rate constants.

Treatment of the kinetics of sequence (1) in isothermal conditions, which leads, for high chemical reactivity of the intermediate B ($k_2 \gg k_1$), to the steady-state approximation with respect to it, i.e. $d[B]/dt = 0$, can be found in the literature [4, 5].

In order to investigate whether this approximation is valid under non-isothermal conditions, we present a kinetic treatment of sequence (1), occurring when the system is heated according to a program whose particular form does not matter for the moment.

Some assumptions have to be made concerning the reaction rate of an elementary reaction r, i.e.:

(i) The reaction rate r of an elementary step depends on two independent variables: concentration [x] and temperature, T, respectively. Mathematically this may be written as

$$r = f([x])k(T) \tag{2}$$

Eq. (2) is considered to have a phenomenological background.

(ii) The functions $f([x])$ and $k(T)$, respectively, are continuous and do not change their sign within the range $(0, t_r)$, where t_r is the time of reaction completion. The first part of this assumption is required in order to ensure that the reaction rate r is continuous along the reaction path and, also, in order to be able to use the integral. The second part of the assumption is, in fact, a restriction on the analytical forms of the two functions, $f([x])$ and $k(T)$.

(iii) The functions k_1 and k_2, respectively, are of the same analytical form and differ only by a scaling constant, i.e. the ratio k_1/k_2 keeps approximately the same value for t ranging from 0 to t_r, where t_r is the time which corresponds to the end of the changes in sequence (1). This assumption is approximately valid if the approximately low range of temperatures within which the reaction occur, $[T(0), T(t_r)]$, is taken into account.

(iv) As far as the initial conditions are concerned, we shall assume that at $t = 0$, $T = T_0$, $[A] = [A(0)]$, $[B(0)] = [C(0)] = 0$, and $[x(t)]$ is the concentration of the compound x which changes in time and temperature.

Under isothermal conditions, the rates of such changes are given by three differential equations [4, 5]. Based on the above assumptions the system of the three differential equations may extend its validity under non-isothermal conditions too, i.e.

$$\begin{aligned} \frac{\mathrm{d}[\mathrm{A}(t)]}{\mathrm{d}t} &= -k_1(t)[\mathrm{A}(t)] \\ \frac{\mathrm{d}[\mathrm{B}(t)]}{\mathrm{d}t} &= k_1(t)[\mathrm{A}(t)] - k_2(t)[\mathrm{B}(t)] \\ \frac{\mathrm{d}[\mathrm{C}(t)]}{\mathrm{d}t} &= k_2(t)[\mathrm{B}(t)] \end{aligned} \tag{3}$$

It has to be noted that, under non-isothermal conditions, the coefficients k_1 and k_2 respectively, are no longer constants, but depend on temperature and, implicitly, on time. System (3) is, thus, a system of differential equations with variable coefficients.

The first equation of system (3) can easily be integrated, leading to

$$\frac{[\mathrm{A}(t)]}{[\mathrm{A}(0)]} = \mathrm{e}^{-\int_0^t k_1(y)\mathrm{d}y} \tag{4}$$

The second equation of the system is a linear first-order differential equation with variable coefficients, whose second term has the well-known solution [6]

$$[\mathrm{B}(t)] = \mathrm{e}^{-\int_0^t k_2(y)\mathrm{d}y}(\textstyle\int_0^t k_1(y)[\mathrm{A}(y)]\mathrm{e}^{\int_0^t k_2(y)\mathrm{d}y}\mathrm{d}y) \tag{5}$$

or, after taking into account Eq. (4) and performing the calculations

$$\frac{[\mathrm{B}(t)]}{[\mathrm{A}(0)]} = \mathrm{e}^{-\int_0^t k_2(y)\mathrm{d}y}(\textstyle\int_0^t k_1(y)\mathrm{e}^{\int_0^t (k_2(y)-k_1(y))\mathrm{d}y}\mathrm{d}y) \tag{6}$$

Once $[\mathrm{A}(t)]$ and $[\mathrm{B}(t)]$ are known, as given by Eqs. (4) and (5), and using the obvious conservation equation

$$[\mathrm{A}(t)] + [\mathrm{B}(t)] + [\mathrm{C}(t)] = [\mathrm{A}(0)] \tag{7}$$

the function $[\mathrm{C}(t)]$ can easily be obtained.

The first average value theorem for definite integrals provides the following equalities

$$\int_0^t k_1(y)\mathrm{d}y = tk_1(\sigma) \tag{8}$$

and respectively

$$\int_0^t k_2(y)\mathrm{d}y = tk_2(\sigma) \tag{9}$$

where $\sigma \in [0, t]$.

According to assumption (iii), "σ" will have the same value for both k_1 and k_2 functions.

With relationships (8) and (9), Eq. (6) becomes

$$\frac{[\mathrm{B}(t)]}{[\mathrm{A}(0)]} = \mathrm{e}^{-tk_2(\sigma)} \int_0^t k_1(y) \mathrm{e}^{t[k_2(\sigma) - k_1(\sigma)]} \mathrm{d}y \tag{10}$$

As

$$\mathrm{e}^{t[k_2(\sigma) - k_1(\sigma)]} \tag{11}$$

is continuous and keeps its sign over the range $[0, t]$, the second average value theorem for definite integrals may also be used in order to calculate the integral of Eq. (10), as shown below

$$\begin{aligned} \int_0^t k_1(y) \mathrm{e}^{t[k_2(y) - k_1(y)]} \mathrm{d}y &= k_1(\sigma) \int_0^t \mathrm{e}^{t[k_2(\sigma) - k_1(\sigma)]} \mathrm{d}y \\ &= \frac{k_1(\sigma)}{k_2(\sigma) - k_1(\sigma)} \mathrm{e}^{t[k_2(\sigma) - k_1(\sigma)]} \end{aligned} \tag{12}$$

By introducing this result into Eq. (10) one obtains

$$\frac{[\mathrm{B}(t)]}{[\mathrm{A}(0)]} = \frac{k_1(\sigma)}{k_2(\sigma) - k_1(\sigma)} \mathrm{e}^{-tk_2(\sigma)} \tag{13}$$

Now, if one takes into consideration that B is a reactive intermediate, i.e.

$$k_2 \gg k_1$$

over the whole time interval $[0, t_r]$, Eq. (13) becomes

$$\frac{[\mathrm{B}(t)]}{[\mathrm{A}(0)]} = \frac{k_1(\sigma)}{k_2(\sigma)} \mathrm{e}^{-tk_1(\sigma)} \tag{14}$$

With this result, the third equation of system (3) becomes

$$\frac{\mathrm{d}[\mathrm{C}(t)]}{\mathrm{d}t} = k_2(t)[\mathrm{A}(0)] \frac{k_1(\sigma)}{k_2(\sigma)} \mathrm{e}^{-k_1(\sigma)t} \tag{15}$$

and, according to assumption (iii), because $k_1(\sigma)/k_2(\sigma) = k_1(t)/k_2(t)$, it follows that

$$\frac{\mathrm{d}[\mathrm{C}(t)]}{\mathrm{d}t} = k_1(t)[\mathrm{A}(0)] \mathrm{e}^{-k_1(\sigma)t} \tag{16}$$

From the first equation of system (3), and also using Eqs. (4) and (8), one obtains

$$\frac{\mathrm{d}[\mathrm{A}(t)]}{\mathrm{d}t} = -k_1(t)[\mathrm{A}(0)] \mathrm{e}^{-k_1(\sigma)t} \tag{17}$$

The differential form of the conservative relationship (7) is

$$\frac{\mathrm{d}[\mathrm{A}(t)]}{\mathrm{d}t} + \frac{\mathrm{d}[\mathrm{B}(t)]}{\mathrm{d}t} + \frac{\mathrm{d}[\mathrm{C}(t)]}{\mathrm{d}t} = 0 \tag{18}$$

By introducing Eqs. (16) and (17) into Eq. (18)

$$\frac{d[B(t)]}{dt} = 0 \qquad (19)$$

i.e. the steady-state approximation is valid even when the kinetic “constants”, k_i, change in time through their change with temperature.

3. Conclusions

By analysing two consecutive first-order reactions, when the system is heated such that the temperature changes in time as $T(t)$, the validity of the steady-state approximation under non-isothermal conditions has been demonstrated. Obviously Eq. (19) is only an approximation as, for its demonstration, we have used assumption (iii) and relationship (14).

References

[1] H.P. Nawada, Thermochim. Acta, 242 (1994) 239.

[2] H. Eyring, J. Walter and G.E. Kimball, Quantum Chemistry, John Wiley & Sons, New York, 1967, p. 308.

[3] E. Segal and C. Popescu, Thermochim. Acta, 247 (1994) 455.

[4] M. Boudart, Kinetics of Chemical Processes, Prentice Hall, Englewood Cliffs, N. J., 1968, p. 63.

[5] P.W. Atkins, Physical Chemistry, Ltd. Edition, Oxford University Press, Oxford, Melbourne, Tokyo, 1990, p. 800.

[6] A.D. Myskis, Introductory Mathematics for Engineers, Mir Publishers, Moscow, 1975, p. 506.