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ON THE VALIDITY OF THE STEADY-STATE APPROXIMATION IN NON-ISOTHERMAL KINETICS
Part III

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Abstract

The authors continue their considerations concerning the validity of the steady-state approximation in non-isothermal kinetics. A sequence of two first-order consecutive reactions with an active intermediate was subjected to kinetic analysis by numerical solution of the corresponding differential kinetic equations for a number of particular cases. The results demonstrated that the rate of change of concentration of the active intermediate is negligibly small if the assumption made in the isothermal case is also accepted for the non-isothermal case, i.e. $k_2(T(t))>>k_1(T(t))$.

Keywords: non-isothermal kinetics, numerical solution of differential kinetic equations, steady-state approximation

Introduction

In part II, a kinetic analysis under non-isothermal conditions was performed for the classical sequence of two first-order consecutive reactions [1]:

$$A \xrightarrow{k_1(T(t))} B \xrightarrow{k_2(T(t))} C \tag{1}$$

where $k_1(T(t))$ and $k_2(T(t))$ are temperature-dependent rate constants. It was shown that the rate of change of concentration of the intermediate B is negligibly small, i.e. $\mathrm{d}[B]/\mathrm{d}t\approx 0$, if the following two assumptions are accepted: (i) $k_2(T(t))>>k_1(T(t))$ and (ii) the ratio $k_1(T(t))/k_2(T(t))$ has approximately the same value throughout the temperature interval in which the reactions occur [1].

Assumption (i) is 'common sense' in chemical kinetics, as it is the essential conditions for high chemical reactivity of intermediate B. Limiting assumption (ii) was introduced as a mathematical restriction in order to avoid the difficulties in integrat-

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ing the system of differential equations with variable coefficients that describes the sequence of reactions (1) under non-isothermal conditions.

Since assumption (ii) is too restrictive, in the present paper we investigate the validity of the steady-state approximation under non-isothermal conditions by taking only assumption (i) into consideration. For this purpose, in a number of particular cases, we find the numerical solutions of the system of differential equations that describe the sequence of reactions (1) under non-isothermal conditions.

Theory

Under non-isothermal conditions, the temperature of the investigated system, T changes in time according to a functional relationship of the form (2)

$$T(t)=\theta(t) \tag{2}$$

where $\theta(t)$ is a continuous function of time. The most usual case corresponds to a linear increase in T with t, i.e.

$$T(t)=T_o+\beta t \tag{3}$$

In the above equation, T_o is the initial temperature and β is the constant heating rate.

The variations in time of the concentrations of the species A, B and C are given by three differential equations [1, 3]:

$$\mathrm{d}[A]/\mathrm{d}t=-k_1(T(t))[A] \tag{4}$$

$$\mathrm{d}[B]/\mathrm{d}t=-k_1(T(t))[A]-k_2(T(t))[A] \tag{5}$$

$$\mathrm{d}[C]/\mathrm{d}t=-k_2(T(t))[B] \tag{6}$$

where the rate constants $k_1(T(t))$ and $k_2(T(t))$ depend on temperature and, implicitly, on time. In order to describe the temperature dependence of the rate constants, the Arrhenius equation is usually used [3], i.e.

$$K_\mathrm{i}(T(t))=A_\mathrm{i}\exp[-E_\mathrm{i}/RT(t)] \quad (i=1,\ 2] \tag{7}$$

The factor A_i is called the pre-exponential factor or the frequency factor, while E_i is called the activation energy.

As the coefficients $k_1(T(t))$ and $k_2(T(t))$ are no longer constants under non-isothermal conditions, Eqs (4), (5) and (6) represent, in fact, a system of three linear differential equations with variable coefficients. Unfortunately, this system has no analytical solution.

This major problem can be bypassed, however, by using, as for the case of isothermal kinetics, the steady-state approximation. According to this, if $k_2(T(t))>>k_1(T(t))$, it may be assumed that the change in rate of the concentration of intermediate B is negligibly small as compared with the changes in rate of the concentrations of reactant A and product C [1, 3]. This may be written as

$$\mathrm{d}[B]/\mathrm{d}t\approx 0 \tag{8}$$

In a previous paper [1], we demonstrated that the steady-state approximation holds as long as $k_2(T(t))/k_1(T(t))>>1$ and keeps a quite constant value. In other words, we showed that, for these two hypotheses, Eq. (8) is obtained.

It must be noted, however, that for isothermal kinetics the same approximation can be demonstrated without the need for the ratio constancy condition. As a result, it seems that the demonstration for the case of non-isothermal kinetics demands an extra restriction. It is the aim of the present work to show, by means of numerical calculations, that this second restrictive condition is not in fact required, and that the steady-state approximation validity is based on the same condition for both isothermal and non-isothermal kinetics.

When the steady-state approximation is taken into account, the discussion of sequence (1) is greatly simplified. Indeed, if condition (8) is used in Eq. (5), and relationship (2) is taken into account, we obtain

$$[B]\approx[k_1(T(t))/k_2(T(t))][A] \tag{9}$$

On substitution of this value of B into Eq. (6), that equation becomes

$$\mathrm{d}[C]/\mathrm{d}t\approx k_1(T(t))[A] \tag{10}$$

and we see that C is formed by a first-order decay of A, with a rate constant $k_1(\theta(t))$, the rate constant of the slower, rate-determining step [3].

Furthermore, if Eq. (5) is taken into account, Eq. (10) can be rewritten in the form

$$\mathrm{d}[C]/\mathrm{d}t\approx-\mathrm{d}[A]/\mathrm{d}t \tag{11}$$

We presume that initially only A is present, and that its concentration is $[A]_o$. In this way, integration of Eq. (11) leads to

$$[A]+[C]\approx[A]_o \tag{12}$$

In order to use Eq. (12), $[A]$ should be determined. For this purpose, Eq. (4) can be integrated, leading to

$$[A]=[A]_o\exp[\int_o^t k_1(T(t))\mathrm{d}t] \tag{13}$$

On substitution of the solution for $[A]$, i.e. Eq. (13), into Eq. (12), the following expression for $[C]$ is obtained:

$$[A]\approx[A]_o\{1-\exp[\int_o^t k_1(T(t))\mathrm{d}t]\} \tag{14}$$

Even though the integral in Eqs (13) and (14) has no exact analytical solution, several approximations with a high degree of accuracy are to be found in the literature [4]. In this paper, the third-degree rational approximation is used [4, 5].

It follows from the foregoing that the sequence of reactions (1) can be described mathematically by more convenient expressions, i.e. Eqs (13) and (14), if the steady-state approximation, i.e. Eq. (8), is accepted. Since Eq. (8) has been demonstrated [1] to hold for the case $k_2/k_1>>1$ and it keeps a fairly constant value throughout the reaction period, it may be stated that sequence (1) can be well described by Eqs (13) and (14) only if the two conditions relating to k_2/k_1 are valid. We have already mentioned that the first condition, $k_2/k_1>>1$, always holds for a reactive intermediate, while the condition of ratio constancy may be considered a restriction. We should now focus our attention on the numerical solution of the system of linear differential equations with variable coefficients, i.e. Eqs (4), (5) and (6), in order to prove that $d[B]/dt\approx 0$ requires only the condition $k_2/k_1>>1$, without any need for the restriction. In other words, Eqs (13) and (14) describe sequence (1) well if B is a reactive intermediate.

From the consideration of particular values for the kinetic parameters, a number of applications are presented below in order to illustrate the correctness of these assumptions.

Application and discussion

As stated in the previous section, Eqs (8) and (14) are approximate expressions whose accuracy is directly related to the magnitude and constancy of the ratio $k_2(T(t))/k_1(T(t))$. We shall attempt to show that the magnitude of the ratio is a sufficient condition for a steady-state approximation, i.e. it is assumed that the higher the value of $k_2(T(t))/k_1(T(t))$, the better the accuracy of the approximation. This assumption can be checked by taking a number of particular values for the kinetic parameters (A_1, A_2, E_1 and E_2) and finding the numerical solutions of the system of three linear differential equations corresponding to Eqs (4)–(6). The results obtained in this way are compared with the results obtained by using the steady-state approximation.

In order to solve the system of differential equations, numerically, and to find the functions $[A]$, $[B]$ and $[C]$, the function NDSolve of the Mathematica® software system is employed [6, 7].

Table 1 Values of the kinetic parameters corresponding to six particular cases

Case	E_1/kJ mol^{-1}	A_1/s^{-1}	E_2/kJ mol^{-1}	A_2/s^{-1}	$\Delta E=E_1-E_2$/kJ mol^{-1}	$\Delta E=/E_1$/%
1	160	$5\cdot 10^{13}$	150	$5\cdot 10^{13}$	10	6.25
2	160	$5\cdot 10^{13}$	145	$5\cdot 10^{13}$	15	9.375
3	160	$5\cdot 10^{13}$	140	$5\cdot 10^{13}$	20	12.5
4	240	$5\cdot 10^{13}$	225	$5\cdot 10^{13}$	15	6.25
5	240	$5\cdot 10^{13}$	217.5	$5\cdot 10^{13}$	22.5	9.375
6	240	$5\cdot 10^{13}$	210	$5\cdot 10^{13}$	30	12.5

For applications, we consider that the temperature changes in time according to Eq. (3), with T_o=298.15 K and β=10 K min^{-1} as particular values. As regards the set of kinetic parameters (A_1, A_2, E_1 and E_2), we shall give special emphasis to the six particular cases presented in Table 1; the initial values $[A]_o$=1 mol l^{-1} and $[B]_o=[C]_o=0$ are taken for every particular case.

Equation (7) allows us to write

$$k_2/k_1=A_2/A_1\exp[-(E_2-E_1)/RT] \tag{15}$$

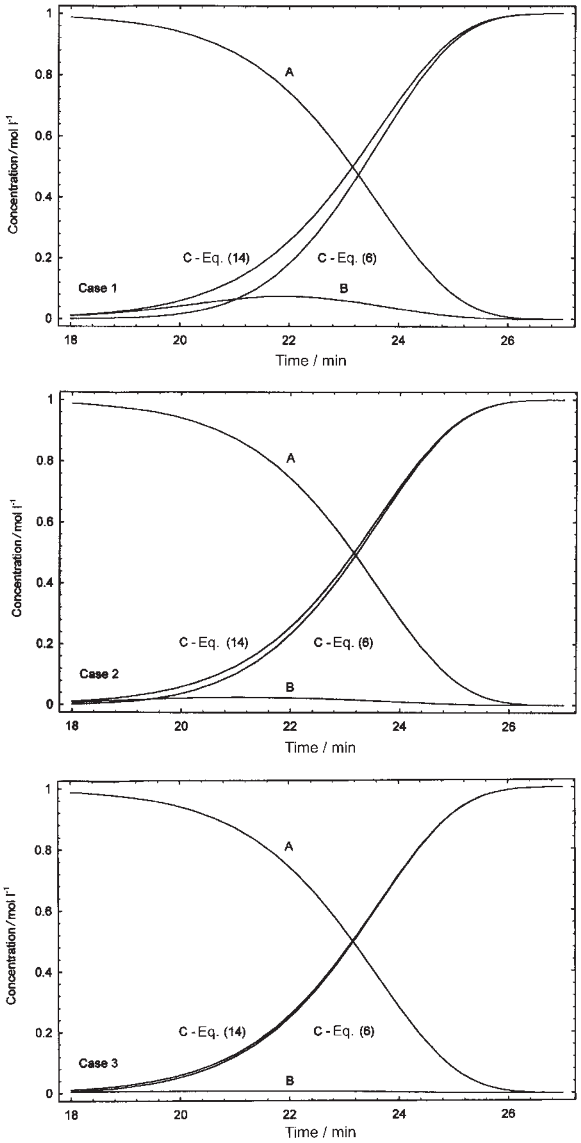

Fig. 1 Variation in time of the concentrations of species *A*, *B* and *C* for cases 1, 2 and 3, as found from numerical integration of Eqs (4)–(6), and for comparison the variation in time of the concentration of *C* given by the approximate Eq. (14) 1a Case 1, 1b Case 2, 1c Case 3

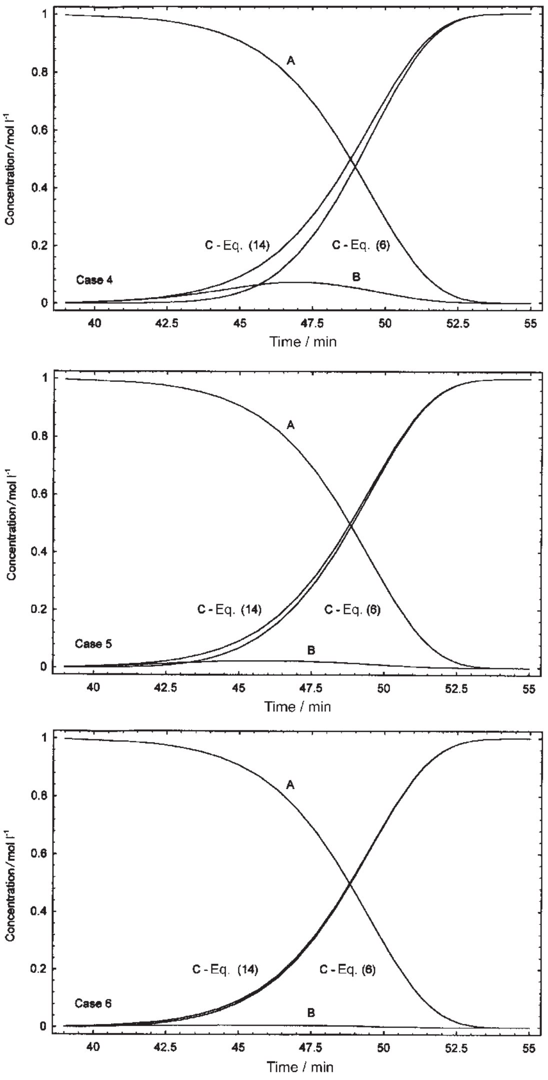

Fig. 2 Variation in time of the concentrations of species *A*, *B* and *C* for cases 1, 2 and 3, as found from numerical integration of Eqs (4)–(6), and for comparison the variation in time of the concentration of *C* given by the approximate Eq. (14) 2a Case 4, 2b Case 5, 2c Case 6

If equal values are chosen for A_1 and A_2 (see Table 1), the ratio k_2/k_1 is related to the value $\Delta E = E_2 - E_1$.

From Table 1, it can be seen that for all cases we consider $A_1 = A_2 = 5 \cdot 10^{13}$ s^{-1} and only the activation energies are changed. For cases 1, 2 and 3, a constant value of $E_1 = 160$ kJ mol^{-1} is considered, while decreasing values of E_2 are taken into account. The results obtained in this way shed light on the influence of increasing $\Delta E = E_1 - E_2$

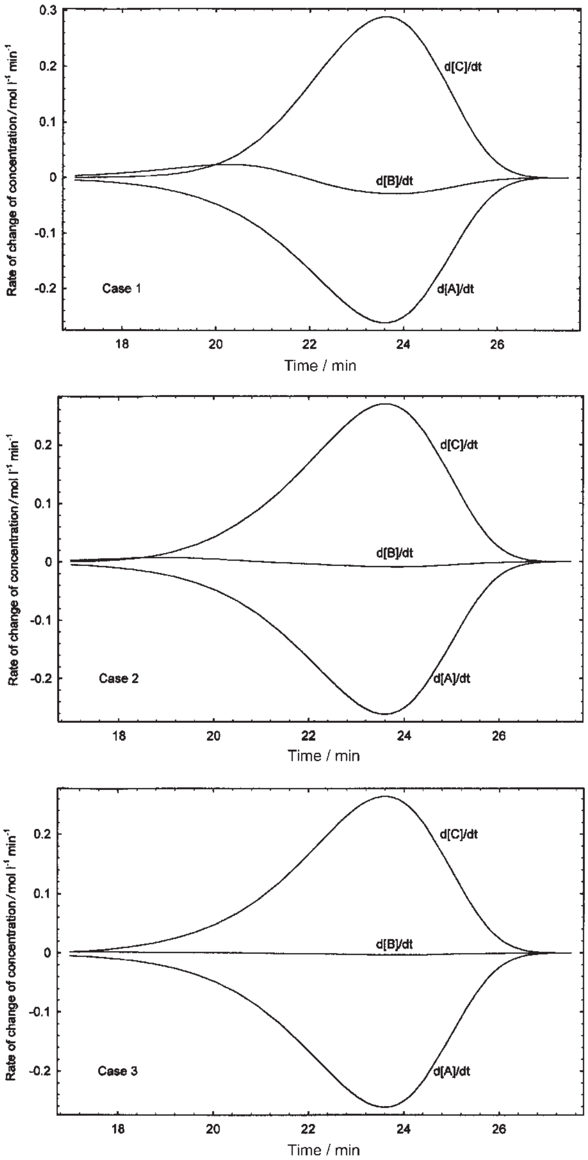

Fig. 3 Variation in time of the rates of change in the concentrations of species A, B and C, as found from numerical integration of Eqs (4)–(6) for cases 1, 2 and 3
3a Case 1, 3b Case 2, 3c Case 3

on the validity of the steady-state approximation. The situation is similar for cases 4, 5 and 6, except that the value of E_1 is taken as 240 kJ mol^{-1}.

The results of the numerical simulations are presented graphically. For cases 1–3 and 4–6, respectively, Figs 1 and 2 show the variations in time of the concentra-

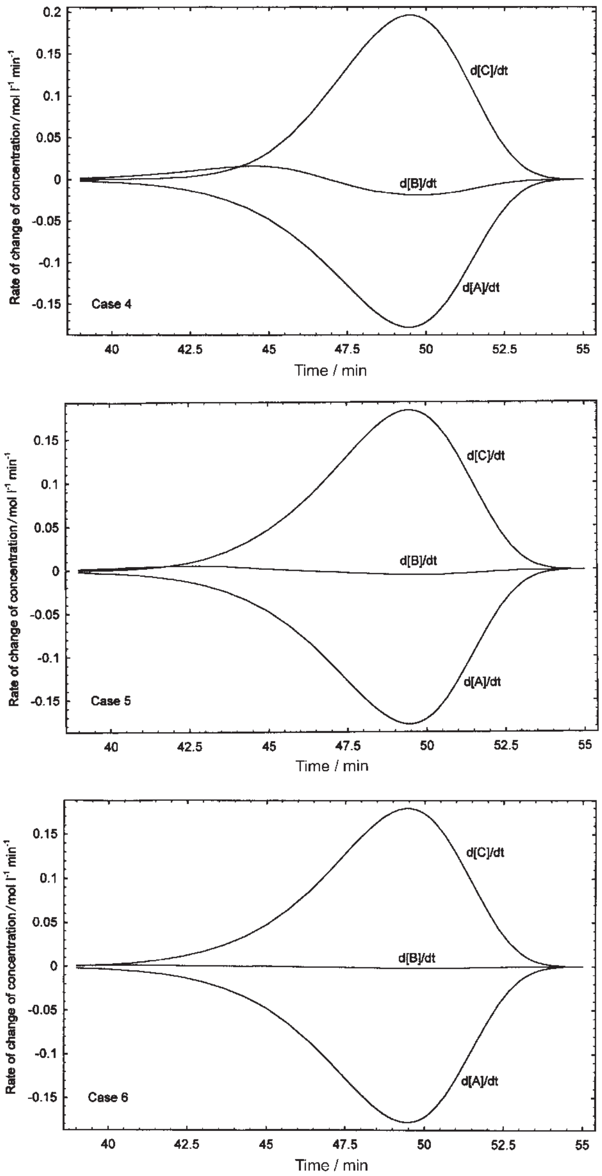

Fig. 4 Variation in time of the rates of change in the concentrations of species A, B and C, as found from numerical integration of Eqs (4)–(6) for cases 4, 5 and 6
4a Case 1, 4b Case 2, 4c Case 3

tions of species A, B and C as found from the numerical integration of Eqs (4)–(6) and, for comparison, the concentration of C given by the approximate Eq. (14). In order to illustrate approximation (8), Figs 3 and 4 show the variations in time of the

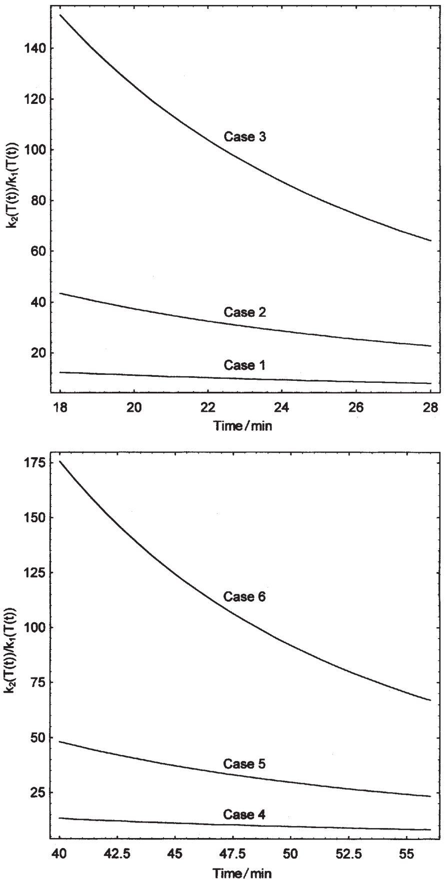

Fig. 5 Variation in time of $k_2(T(t))/k_1(T(t))$ for cases 1–6, 5a Cases 1–3, 5b Cases 4–6

rates of change in the concentrations of species A, B and C as found from the numerical integration of Eqs (4)–(6), i.e. the evolution of d[A]/dt, d[B]/dt and d[C]/dt, corresponding to all of the cases listed in Table 1. Additionally, Fig. 5 depicts the variation in time of $k_2(T(t))/k_1(T(t))$ for cases 1–6.

The presented results permit a number of inferences.

1. For a given value of E_1, the higher the value of the difference (E_1–E_2), the higher the accuracy of approximation (8). For a given value of E_1, the higher the value of the difference (E_1–E_2), the more precise the description of the variation in time of the concentration of C given by Eq. (14).

2. The validity of Eqs (8) and (14) seems to be related to the quantity $(E_1-E_2)/E_1$ and not to the absolute difference E_1–E_2 if different values of E_1 are considered, i.e. the higher the value of $(E_1-E_2)/E_1$, the greater the accuracy of approximations (8) and (14).

3. The higher the quantity $(E_1–E_2)/E_1$, the higher the ratio of the two kinetic constants $k_2(T(t))/k_1(T(t))$. It can therefore be considered that under non-isothermal conditions the steady-state approximation is also valid if the ratio of the kinetic constants satisfies the condition $k_2(T(t))/k_1(T(t))>>1$.

The last two results indicate that, although Eq. (15) suggests that this ratio of the two constant rates should depend only on ΔE, the accuracy of the steady-state approximation also seems to be related to the ratio $\Delta E/E_1$.

Conclusions

The validity of the steady-state approximation under non-isothermal conditions has been tested by analysing a sequence of two consecutive first-order reactions with an active intermediate. It has been shown by numerical simulation that the accuracy of the approximate Eqs (8) and (14) can be considered satisfactory if the ratio of the two kinetic constants satisfies the condition $k_2(T(t))/k_1(T(t))>>1$, this condition being related to the quantity $(E_1–E_2)/E_1$ if the pre-exponential factors of the two reactions are equal.

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