

ON THE VALIDITY OF THE STEADY-STATE APPROXIMATION IN NON-ISOTHERMAL KINETICS Part IV. The case of constant rate thermal analysis

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Abstract

The paper investigates the validity of steady-state approximation for the case of constant rate thermal analysis experiments. It is shown that the approximation holds for the experiments run with a controlled rate of either the decomposition of the compound, or the production of gas.

Keywords: constant rate thermal analysis, non-isothermal kinetics, steady-state approximation

Introduction

Following previous work on the validity of the steady-state approximation (SSA) in non-isothermal kinetics [1–3], the present paper deals with the requirements of controlled rate thermal experiments.

Let us consider again the classical reaction sequence



where B* is the reactive intermediate, and k_1 and k_2 are the reaction rate constants. The SSA states that the concentration of the reactive intermediate B* is very low as compared with that of the stable species, and its variation is almost nil [4].

The corresponding three differential equations which describe the evolution of reaction sequence (1) are

$$\frac{da}{dt} = -k_1a \quad (2)$$

$$\frac{db}{dt} = k_1a - k_2b \quad (3)$$

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$$\frac{dc}{dt} = k_2 b \quad (4)$$

where a , b and c denote the normalized concentrations of species A, B and C, i.e. $a=[A]/[A]_0$; $b=[B^*]/[A]_0$; $c=[C]/[A]_0$; $[A]$, $[B^*]$ and $[C]$ being the concentrations of compounds A, B^* and C at moment t , and $[A]_0$ being the initial concentration of compound A.

The fact that B^* is the reactive intermediate requires

$$k_2 \gg k_1 > 0 \quad (5)$$

and the mass conservation law leads to

$$a + b + c = 1 \quad (6)$$

or its differential form

$$\frac{da}{dt} + \frac{db}{dt} + \frac{dc}{dt} = 0 \quad (6')$$

Also, if it is taken into account that the experiment is a non-isothermal one, the two 'rate constants' are time-dependent, and thus the above equations have variable coefficients. The general conditions that must hold for the solution of Eqs (2)–(6) to be obtained have been discussed previously [2, 3].

Let us consider now that the experiment is run at a constant rate. In this case, we have either

$$\frac{da}{dt} = \text{constant} = -K \quad (7)$$

or

$$\frac{dc}{dt} = \text{constant} = K \quad (8)$$

which means generally that we control either the rate of decomposition of the initial compound (Eq. (7)), or the rate of product formation (Eq. (8)).

Case I – Control of the rate of decomposition of the initial compound

In this case, Eqs (2)–(6) become

$$\frac{da}{dt} = -K \quad (2')$$

$$\frac{db}{dt} = K - k_2(t)b \quad (3')$$

$$\frac{dc}{dt} = k_2(t)b \quad (4')$$

$$k_2 \gg k_1 \quad (5')$$

$$-K + \frac{db}{dt} + \frac{dc}{dt} = 0 \quad (6'')$$

Equation (3') may be rewritten as

$$\frac{db}{dt} + k_2(t)b = K$$

the solution of which [5] is

$$b = \exp\left(-\int_0^t k_2(t)dt\right) \left[\int_0^t K \exp\left(\int_0^t k_2(t)dt\right) dt \right] \quad (9)$$

From the first mean theorem for the definite integrals, we may write [6]

$$\int_0^t k_2(t)dt = k_2(\xi)t, \quad \xi \in [0, t] \quad (10)$$

Substitution of Eq. (10) into (9) and the subsequent calculations lead to

$$b = \frac{K}{k_2(\xi)} [1 - \exp(-k_2(\xi)t)] \quad (11)$$

For time periods during which the steady state is reached, we may assume that

$$tk_2(\xi) \gg 0 \quad (12)$$

and consequently $\exp(-k_2(\xi)t) \rightarrow 0$. With this result, Eq. (11) becomes

$$b \approx \frac{K}{k_2(\xi)} = \text{constant} \quad (13)$$

Substitution of Eq. (13) into (3') lead to

$$\frac{db}{dt} = K - k_2(t) \frac{K}{k_2(\xi)} \approx 0 \quad (14)$$

It may be noted that the constancy of the intermediate compound concentration, b , was obtained regardless of the values of k_1 and K .

From Eq. (13), taking into account relationship (12), and also considering that K has a low value, we obtain that the concentration of B is negligibly low, i.e.

$$b \approx 0 \quad (15)$$

It is noteworthy that the fact that the concentration of the reactive compound is very low depends on the value of K .

Case II – Control of the rate of product formation

In this case, Eqs (2)–(6) become

$$\frac{da}{dt} = -k_1(t)a \quad (2'')$$

$$\frac{db}{dt} = k_1(t)a - K \quad (3'')$$

$$\frac{dc}{dt} = K \quad (4'')$$

$$k_2(t) \gg k_1(t) > 0 \quad (5'')$$

$$\frac{da}{dt} + \frac{db}{dt} + K = 0 \quad (6'')$$

Comparison of Eqs (4) and (4'') furnishes

$$b = \frac{K}{k_2(t)} \quad (16)$$

The value of concentration ' b ' may also be calculated from Eq. (3'') by integration. This results in

$$b = \int_0^t k_1(t) \exp\left(-\int_0^t k_1(t) dt\right) dt - Kt \quad (17)$$

The comparison of Eqs (16) and (17) allows the value of the integral to be inferred as

$$\int_0^t \left[k_1(t) \exp\left(-\int_0^t k_1(t) dt\right) \right] dt = K \frac{tk_2(t) + 1}{k_2(t)} \approx Kt \quad (18)$$

where, to approximate the value of the term in brackets, we have taken into account that for the long time periods required for the system to reach the steady state, $tk_2(t) \gg 1$.

With this result, Eq. (17) becomes

$$b \approx 0 \quad (19)$$

which means that the concentration of the intermediate compound is negligibly low.

The results given by Eqs (15) and (19) allow the conclusion that the SSA maintains its validity for processes run under non-isothermal conditions with a controlled rate of either the decomposition of a compound, or the production of gas.

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