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STEADY-STATE APPROXIMATION. 5

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Abstract

The example of the sequence of reactions

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

and the steady-state approximation are used to present a demonstration of the fact that the evolution of the reaction rates under non-isothermal conditions depends on the ratio of the activation energies and on the heating rate. At the same time, it is shown that, under isothermal conditions, the ratio of the activation energies plays no role.

Keywords: activation energy, non-isothermal kinetics, steady-state approximation

Introduction

Following our previous researches dealing with the steady-state approximation [1, 2], a numerical simulation of the reaction sequence
under non-isothermal conditions suggested that the time evolution of the reaction rates

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

v_a, v_b and v_c might depend on the ratio of the activation energies E_1/E_2. This result is somewhat surprising: for the demonstration of the steady-state approximation, the condition is

$$\frac{k_1}{k_2} << 1 \tag{1}$$

The Arrhenius form of the reaction rate constants k_1 and k_2, leads to

$$\frac{k_1}{k_2} = \frac{A_1}{A_2}\exp\left(-\frac{E_1 - E_2}{RT}\right) << 1 \tag{2}$$

and indicates that the activation energy difference, $\Delta E = E_1 - E_2$, plays an important role.

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The present work has the aim of establishing theoretical support for the importance of the activation energy ratio under non-isothermal conditions.

Theory

Let us consider the system of differential equations describing the reaction sequence (I)

$$\begin{aligned} v_a &= \frac{da}{dt} = -k_1 a \\ v_b &= \frac{db}{dt} = k_1 a - k_2 b = k_1 a\left(1 - \frac{k_2 b}{k_1 a}\right) \\ v_c &= \frac{dc}{dt} = k_2 b \end{aligned} \tag{3}$$

According to the steady state approximation [3]

$$v_b \approx 0 \tag{4}$$

It is obvious that, if the value of v_b at the extremum is close to zero

$$v_b|_{\text{extremum}} \approx 0 \tag{5}$$

then condition (4) will be fulfilled.

The extremum value of v_b requires the calculation of its first derivative

$$\frac{dv_b}{dt} = \frac{dk_1}{dt}a + k_1\frac{da}{dt} - \frac{dk_2}{dt}b - k_2\frac{db}{dt} \tag{6}$$

and the extremum is found for the known condition

$$\frac{dv_b}{dt} = 0 \tag{7}$$

Isothermal case

Under isothermal conditions

$$\frac{dk_1}{dt} = \frac{dk_2}{dt} = 0 \tag{8}$$

and Eq. (6) becomes

$$\frac{dv_b}{dt} = k_1\frac{da}{dt} - k_2\frac{db}{dt} \tag{9}$$

By replacing da/dt and db/dt with their expressions from system (3), we obtain

$$\frac{\mathrm{d}v_b}{\mathrm{d}t} = k_1(-k_1a) - k_2(k_1a - k_2b) = -k_1^2a - k_1k_2a + k_2^2b \tag{10}$$

The condition for the extremum, Eq. (7), turns Eq. (10) into

$$k_2^2b = k_1^2a + k_1k_2a \tag{11}$$

or, after rearrangement of the terms

$$\frac{b}{a}\Big|_{\text{extremum}} = \frac{k_1}{k_2}\left(\frac{k_1}{k_2} + 1\right) \tag{12}$$

With regard to the condition (Eq. (1)) that B is a reactive intermediate, Eq. (12) becomes

$$\frac{b}{a}\Big|_{\text{extremum}} \approx \frac{k_1}{k_2} \tag{13}$$

This result may be used to calculate the value of $v_b|_{\text{extremum}}$ from its expression in system (3)

$$v_b|_{\text{ext}} = k_1a\left(1 - \frac{k_2b}{k_1a}\Big|_{\text{ext}}\right) = 0 \tag{14}$$

Equation (14) shows that, under isothermal conditions, the value of v_b at the extremum point is equal to zero, provided that the approximation of the reactive intermediate (Eq. (13)) is accepted. It may be noted that, under isothermal conditions, the ratio of the activation energies does not play any role.

Non-isothermal case

Under non-isothermal circumstances, differentiation of either of the two kinetic constants k gives

$$\frac{\mathrm{d}k}{\mathrm{d}t} = \frac{\beta E}{T^2R}k \tag{15}$$

where $\beta=\mathrm{d}T/\mathrm{d}t$ is the heating rate. If Eq. (15) is taken into account, Eq. (7) leads to

$$\frac{\mathrm{d}v_b}{\mathrm{d}t} = \frac{\beta}{T^2}\left(ak_1\frac{E_1}{R} - bk_2\frac{E_2}{R}\right) + k_2^2b - k_1k_2a\left(1 + \frac{k_1}{k_2}\right) = 0 \tag{16}$$

Equation (1), the condition of the reactive intermediate, means that

$$1 + \frac{k_1}{k_2} \approx 1$$

and Eq. (16) may be rearranged into

$$\frac{k_2b}{k_1a}\Big|_{\mathrm{ext.}}=\frac{\dfrac{\beta E_1}{T^2R}-k_2}{\dfrac{\beta E_2}{T^2R}-k_2} \qquad (17)$$

Equation (17) now allows the calculation of $v_b|_{\mathrm{ext}}$ from the expression given in system (3). After rearrangement of the terms, we obtain

$$v_b|_{\mathrm{ext.}}\int_0^1 x\,\mathrm{d}x=k_1a\frac{\dfrac{\beta E_2}{T^2R}\left(1-\dfrac{E_1}{E_2}\right)}{\dfrac{\beta E_2}{T^2R}-k_2} \qquad (18)$$

Equation (18) clearly shows that the value of v_b at the extremum depends on the ratio of the activation energies, E_1/E_2, as was observed from the numerical simulation. It may also be noted that the heating rate influences the value of v_b.

References

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