

# Conservation Laws for Chemical Reactions in a Plate Reactor with Diffusion and Convection

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**Abstract:** Concentration and temperature conservation laws (CL) for chemical reactions occurring in nonstationary regimes of a plate reactor with diffusion and convection are investigated. Two types of CL are distinguished – autonomous (independent) and non-autonomous (dependent) on time, length, and with of the reactor. The dependence of these laws on the rate of the reaction flow and the diffusion coefficients of reagents and thermal diffusion has been established. It is shown that the autonomous laws are fulfilled only with uniform diffusion of all reactants and convection. Examples of the use of these CL for checking the correspondence of experimental data to the supposed stepwise mechanisms of reactions proceeding according to arbitrary kinetic laws are given.

**Keywords:** chemical reactions; plate reactor with diffusion and convection; autonomous and non-autonomous conservation laws.

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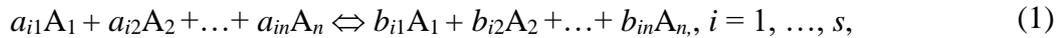
## 1. Introduction

Conservation laws (CL) underlie physicochemical and biological processes and express the most important constant (invariant) connections between the substances and energy involved. The simplest by-shape CL is characteristic of closed spatially homogeneous (lumped) systems [1,2]. In open spatially inhomogeneous (distributed) systems, CL can be preserved, changed, partially and completely disturbed, or remain unknown. Chemical processes in distributed systems are described by models considering the diffusion of substances and the convection of heat [3-9]. These models are multidimensional systems of nonlinear partial differential equations of mathematical physics, which, as a rule, cannot be exactly solved [10]. For such equations, exact CL (exact invariants), which are strictly constant expressions based on the solutions of these equations, is rather difficult to construct, and developing methods for establishing them is an urgent problem. Currently, the literature describes only exact CL for chemical reactions with ideal kinetics based on the law of mass action (LMA) occurring in reactors of ideal mixing and displacement [11] or exact CL (full invariants) [12] for some types of incompletely mixed reactors without diffusion or with one-dimensional diffusion [13,14]. In this regard, this work aims to develop methods for establishing new concentration and concentration-temperature CL for chemical reactions proceeding unsteadily in an open nonisothermal plate reactor, taking into account the two-dimensional diffusion of reagents and the convection of heat in longitudinal and transverse directions. In practice, such CL can be used to increase the reliability of solving the inverse problem of chemical kinetics [15-27],

associated with the refinement of the stepwise mechanism of a chemical reaction proceeding according to unknowns, including nonideal (Marceline de Donde kinetics, etc.) kinetic laws.

## 2. Theoretical Part

Let the chemical reaction proceed through the elementary stages



where  $i$  is the number of the stage;  $s$  is the number of stages;  $a_{ij}$ ,  $b_{ij}$  are the stoichiometric coefficients of the reagents  $A_j$ ;  $j = 1, \dots, n$  – reagent number;  $n$  is the number of reagents. The unsteady flow of such a reaction according to an arbitrary kinetic law in an open plate nonisothermal reactor with a nonuniform distribution of reagent concentrations and temperature over time, along the length and of the reactor, is described by a system of nonlinear partial differential equations that cannot be solved exactly [3-10]:

$$\partial A_j / \partial t + q(\partial A_j / \partial x + \partial A_j / \partial y) = \sum_i (b_{ij} - a_{ij})r_i + D_j(\partial^2 A_j / \partial x^2 + \partial^2 A_j / \partial y^2), \quad j = 1, \dots, n \quad (2)$$

$$\partial \theta / \partial t + q(\partial \theta / \partial x + \partial \theta / \partial y) = \sum_i Q_i r_i + \beta(\theta_x - \theta) + D_\theta(\partial^2 \theta / \partial x^2 + \partial^2 \theta / \partial y^2) \quad (3)$$

where  $A_j(x, y, t)$  are the current concentrations of reagents, mole fractions;  $x$  is the current length of the reactor, no size;  $y$  is the current width of the reactor, no size;  $t$  is the current time,  $s$ ;  $q$  – rate of the reaction flow,  $1/s$  ( $q = 0$  – closed reactor);  $r_i = r_i(k_{\pm i}, A_j, \theta)$  – the rates of the stages according to some arbitrary (including nonideal) kinetic law;  $k_{\pm i}$  – unknown stage rate constants;  $\theta(x, y, t)$  is the current relative temperature (the ratio of the current temperature  $T(x, y, t)$  to the initial  $T^0$ , K), no size;  $Q_i$  – relative heat effects of stages, no size;  $\beta$  – coefficient of heat transfer through the reactor wall ( $\beta = 0$  – adiabatic reactor,  $\beta \neq 0$  – non-adiabatic reactor),  $1/s$ ;  $\theta_x$  – reactor wall temperature, no size;  $D_j$  and  $D_\theta$  – coefficients of diffusion of reagents and thermal diffusion,  $1/s$ .

Let us define the initial conditions (i.c.)

$$A_j(x, y, 0) = A_j^0, \quad \theta(x, y, 0) = \theta^0 \quad (4)$$

where  $A_j^0$ ,  $\theta^0$  are constants. Let us accept the boundary conditions (b.c.)

$$A_j(0, y, t) = A_j(x, 0, t) = A_j^0, \quad \theta(0, y, t) = \theta(x, 0, t) = \theta^0 \quad (5)$$

$$\partial A_j(1, y, t) = \partial A_j(x, 1, t) = 0, \quad \partial \theta(1, y, t) = \partial \theta(x, 1, t) = 0$$

In an isothermal plate reactor, equation (3) with the corresponding i.c. and b.c. are not used. Let us determine and compare the following from (1)-(5) spatial-temporal distributions of concentrations, temperatures, and corresponding CL for different values of the reactor parameters, diffusion, and convection coefficients.

For a closed ( $q = 0$ ) non-adiabatic ( $\beta \neq 0$ ) reactor in the absence of diffusion and convection ( $D_j = D_\theta = 0$ ), equations (2)-(3), taking into account the laws of mass conservation, take the form

$$\sum_j \alpha_{mj} \partial A_j / \partial t = 0, \quad m = 1, 2, \dots, N \quad (6)$$

where  $\alpha_{mj}$  are constants determined by the stoichiometry of the stages;  $N = n - P$ ;  $P$  – the rank of the matrix of stoichiometric coefficients ( $b_{ij} - a_{ij}$ ). For a closed adiabatic reactor ( $\beta = 0$ ), taking into account the law of conservation of heat, one more equation is fulfilled

$$\partial(\sum_j \beta_j A_j + \theta) / \partial t = 0 \quad (7)$$

where  $\beta_j$  are constants depending on the stoichiometry and thermal effects of the stages. System (6)-(7) qualitatively differs from the original  $(n+1)$ -dimensional nonlinear system of interdependent equations (2)-(3) in that it consists of a smaller number  $N+1$  linear with respect

to algebraic sums (we call them complexes) concentrations and the temperature of independent (over complexes) equations, each of which is solved exactly. The solutions of these differential equations express autonomous (independent of time and space) independent stoichiometric concentration and concentration-temperature CL in the algebraic form [2, 8, 11]:

$$K_m(x, y, t) \equiv \sum_j \alpha_{mj} A_j(x, y, t) = \sum_j \alpha_{mj} A_j^0, m = 1, 2, \dots, N \tag{8}$$

$$L(x, y, t) \equiv \sum_j \beta_j A_j(x, y, t) + \theta(x, y, t) = \sum_j \beta_j A_j^0 + \theta^0 \tag{9}$$

For an open ( $q \neq 0$ ) plate reactor with uniform diffusion and convection ( $D_j = D_0 \equiv D$ ), differential relations of the form (6)-(7) take the form

$$\partial K_m / \partial t + q(\partial K_m / \partial x + \partial K_m / \partial y) = D(\partial^2 K_m / \partial x^2 + \partial^2 K_m / \partial y^2), m = 1, 2, \dots, N \tag{10}$$

$$\partial L / \partial t + q(\partial L / \partial x + \partial L / \partial y) = D(\partial^2 L / \partial x^2 + \partial^2 L / \partial y^2) \tag{11}$$

In an isothermal plate reactor with uniform diffusion, only equalities (10) are satisfied. Each of these equations is also independent of the form of the kinetic law and is equivalent to a diffusion equation of the form  $z'_t + q(z'_x + z'_y) = z''_{xx} + Dz''_{yy}$ , where  $z$  is a complex. Such equations reduce to three ordinary differential equations [10] and have exact solutions of the form  $z(x, y, t) = [C_1 \exp(\lambda_1 x) + C_2 \exp(\lambda_2 x)] [C_3 \exp(\lambda_3 y) + C_4 \exp(\lambda_4 y)] C_5 \exp(-\lambda_5 t)$ , which, taking into account (4)-(5), take the trivial form  $z(x, y, t) = z(0, 0, 0)$ , where  $\lambda_{1,2} \equiv [q \pm (q^2 - 4\rho_1^2)^{1/2}] / 2$ ,  $\lambda_{3,4} \equiv [q \pm (q^2 - 4\rho_2^2)^{1/2}] / 2$ ,  $\lambda_5^2 = \rho_1^2 + \rho_2^2$ ,  $\rho_1, \rho_2 > 0$ ,  $C_1, C_2, C_3, C_4, C_5$  are constants.

As applied to equations (10)-(11), this means that their trivial solutions also coincide with autonomous CL (8)-(9), which are also valid for uniform diffusion (convection) and also do not depend on the form of the kinetic law. Because these CL depend only on the stoichiometry of the stages and i.c. reaction (1), then all linear-dependent reaction mechanisms with any number of stages are characterized by the same number of independent autonomous CL, which can be reduced to the same form. Consequently, only linearly independent mechanisms of reaction (1) can be unambiguously identified using autonomous CL with uniform diffusion (convection) and any kinetic law.

In closed and open plate reactors with nonuniform diffusion and convection ( $D_j \neq D_0 \neq D$ ), relations (6)-(9) are violated «in proportion» to the intensity of diffusion and convection. In this case, the diffusion-homogeneous complexes  $K_m$  and  $L$  in the right-hand sides of equations (10)-(11) are replaced by diffusion-inhomogeneous complexes:

$$\partial K_m / \partial t + q(\partial K_m / \partial x + \partial K_m / \partial y) = \partial^2 M_m / \partial x^2 + \partial^2 M_m / \partial y^2, m = 1, 2, \dots, N \tag{12}$$

$$\partial L / \partial t + q(\partial L / \partial x + \partial L / \partial y) = \partial^2 P / \partial x^2 + \partial^2 P / \partial y^2 \tag{13}$$

where  $M_m(x, y, t) \equiv \sum_j \alpha_{mj} D_j A_j$ ,  $P(x, y, t) \equiv \sum_j \beta_j D_j A_j(x, y, t) + D_0 \theta(x, y, t)$  – diffusion-inhomogeneous complexes. In an isothermal plate reactor with nonuniform diffusion, only equalities (12) are satisfied. The system of equations (12)-(13) also does not depend on the form of the kinetic law and describes the evolution of the CL for the reaction proceeding according to the mechanism (1) in a nonisothermal open reactor with diffusion and convection of arbitrary intensity. However, the number of equations of this system  $N+1$  is less than the number of unknowns  $n+1$ , and it has many solutions. To obtain an unambiguous solution, let us supplement it with  $n-N$  with any of the original equations (2)-(3), set any specific form of the kinetic law (for example, the law of mass action, LMA) and low stage velocities ( $r_i \sim 0$ ). The analysis showed that, under such conditions, the solution found weakly depends on the form of the kinetic law and makes it possible to fairly accurately calculate non-autonomous

CL, which can be used to refine the reaction mechanisms taking into account possible nonuniform diffusion and convection.

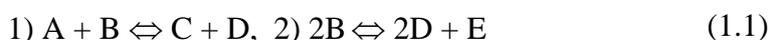
The CL cannot be fully plotted for a plate reactor with longitudinal and radial diffusion are hypersurfaces in four-dimensional space. On three-dimensional plots of the dependences of complexes, for example, on time and length (with a fixed width), autonomous CL looks like horizontal planes, and non-autonomous ones - like curved surfaces. On two-dimensional plots, for example, versus time (with fixed length and width), they respectively represent horizontal and curved lines touching the corresponding horizontal straight lines near i.c.

We emphasize once again that an important difference between equations of the form (10)-(11) and (12)-(13), following from the original equations (2)-(3), is that they are valid for any kind of kinetic law, and, consequently, on the rate constants of the stages of the reaction mechanism (1). The solutions of such equations express various autonomous and non-autonomous CL, which can be found exactly with uniform diffusion and convection. In the case of nonuniform diffusion and convection, these solutions are known exactly only in normal conditions but can be calculated numerically at any point (as described above). Autonomous CL, in contrast to non-autonomous CL, depends only on the stoichiometry of the stages and i.c. reaction, which is especially convenient for solving the inverse problem of choosing the most probable of several alternative mechanisms for the occurrence of chemical reactions with unknown kinetic laws and rate constants of the stages, which is often encountered in practice. Note that CL allows one to solve another type of inverse problem – to determine reagents with equal (taking into account measurement errors) diffusion coefficients according to the following rule (we shall call it invariant): «If a non-autonomous CL coincides with the corresponding autonomous CL, then the reagents included in it are characterized by practically equal diffusion coefficients».

For experimental verification of the studied reaction mechanism, it is sufficient to measure the values of the concentrations of reagents and temperatures at different times in any section of the reactor (for example, at the outlet) and check the validity of equalities (8) and (12) in an isothermal reactor and additionally equalities (9) and (13) in a nonisothermal reactor (as described above). If all of them are fulfilled (taking into account measurement errors), then the proposed mechanism adequately describes the regularities of the reaction. If at least one of these relationships is violated (with excess measurement errors), the studied reaction mechanism does not correspond to the experimental data. To increase the solution's reliability to the inverse problem, it is recommended to check the found CL for different i.c. Let us apply the method described above to analyze the mechanisms of different reactions.

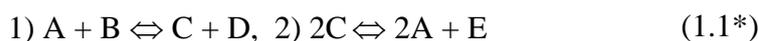
### 3. Computational Experiment

Example 1. The reaction of obtaining 4-tert-butylpyrocatechol (4-TBPC) by oxidation of 4-tert-butylphenol (4-TBP) with hydrogen peroxide in the presence of titanosilicate catalysts was experimentally studied in [28,29] in a nonstationary mode of a closed isothermal plate reactor. In these works, an ideal kinetic LMA was postulated, and the following two-stage reaction mechanism was proposed



where A – 4-TBP ( $C_{10}H_{14}O$ ), B – hydrogen peroxide ( $H_2O_2$ ), C – 4-TBPC ( $C_{10}H_{14}O_2$ ), D –  $H_2O$ , E –  $O_2$ . However, theoretically, there are many alternative mechanisms of this reaction

involving the same reagents and the stage  $2C \Leftrightarrow 2A + E$  ( $2C_{10}H_{14}O_2 \Leftrightarrow 2C_{10}H_{14}O + O_2$ ), for example:



Let us compare these mechanisms with the help of the CL for an arbitrary kinetic law. Let us write for each of their equations (2)-(3) in a closed ( $q = 0$ ) isothermal ( $\theta = \theta^0$ ) plate reactor, taking into account the diffusion of reagents

$$\partial A/\partial t = -r_1 + D_A(\partial^2 A/\partial x^2 + \partial^2 A/\partial y^2), \quad \partial B/\partial t = -r_1 - 2r_2 + D_B(\partial^2 B/\partial x^2 + \partial^2 B/\partial y^2) \quad (1.2)$$

$$\partial C/\partial t = r_1 + D_C(\partial^2 C/\partial x^2 + \partial^2 C/\partial y^2), \quad \partial D/\partial t = r_1 + 2r_2 + D_D(\partial^2 D/\partial x^2 + \partial^2 D/\partial y^2), \quad (1.2^*)$$

$$\partial E/\partial t = r_2 + D_E(\partial^2 E/\partial x^2 + \partial^2 E/\partial y^2),$$

$$\partial A/\partial t = -r_1 + 2r_2 + D_A(\partial^2 A/\partial x^2 + \partial^2 A/\partial y^2), \quad \partial B/\partial t = -r_1 + D_B(\partial^2 B/\partial x^2 + \partial^2 B/\partial y^2),$$

$$\partial C/\partial t = r_1 - 2r_2 + D_C(\partial^2 C/\partial x^2 + \partial^2 C/\partial y^2), \quad \partial D/\partial t = r_1 + D_D(\partial^2 D/\partial x^2 + \partial^2 D/\partial y^2),$$

$$\partial E/\partial t = r_2 + D_E(\partial^2 E/\partial x^2 + \partial^2 E/\partial y^2)$$

where  $A, B, C, D$ , and  $E$  are the concentration of reagents;  $r_1, r_2$  – any kinetic functions. Hence, taking into account (6)-(9), it follows that for each of them under any kinetic law and uniform diffusion, the same three ( $P = 2, N = 5 - 2 = 3$ ) autonomous independent concentration CL of the form (8), which are expressed through the same complexes

$$K_1(x, y, t) \equiv A(x, y, t) + C(x, y, t) = A^0 + C^0 \quad (1.3)$$

$$K_2(x, y, t) \equiv B(x, y, t) + D(x, y, t) = B^0 + D^0,$$

$$K_3(x, y, t) \equiv B(x, y, t) + C(x, y, t) + 2E(x, y, t) = B^0 + C^0 + 2E^0.$$

For i.c.  $A_0=1, B_0=1, C_0=D_0=E_0=0$  and the right-hand sides of these CL coincide

$$K_1(x, y, t) \equiv A + C = 1, \quad K_2(x, y, t) \equiv B + D = 1, \quad K_3(x, y, t) \equiv B + C + 2E = 1 \quad (1.4)$$

As noted above, this is due to the fact that these mechanisms consist of linearly dependent stages and cannot be unambiguously identified using autonomous CL with uniform diffusion and any kinetic law.

In a plate reactor with nonuniform diffusion and convection, equalities (1.3)-(1.4) are violated, CL becomes non-autonomous and are described by equations of the form (12):

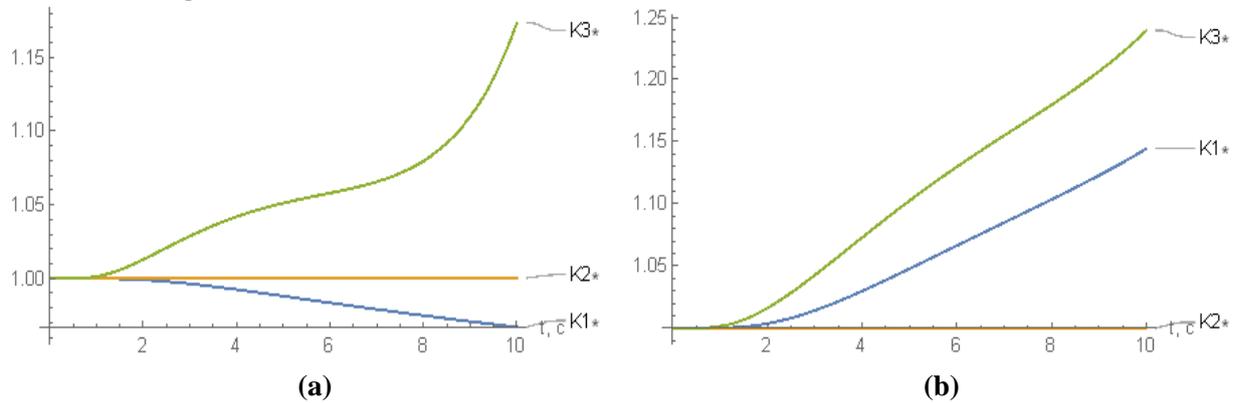
$$\partial K_1/\partial t + q(\partial K_1/\partial x + \partial K_1/\partial y) = \partial^2 M_1/\partial x^2 + \partial^2 M_1 A/\partial y^2 \quad (1.5)$$

$$\partial K_2/\partial t + q(\partial K_2/\partial x + \partial K_2/\partial y) = \partial^2 M_2/\partial x^2 + \partial^2 M_2 A/\partial y^2$$

$$\partial K_3/\partial t + q(\partial K_3/\partial x + \partial K_3/\partial y) = \partial^2 M_3/\partial x^2 + \partial^2 M_3 A/\partial y^2$$

here  $M_1(x, y, t) \equiv D_A A(x, y, t) + D_C C(x, y, t)$ ,  $M_2(x, y, t) \equiv D_B B(x, y, t) + D_D D(x, y, t)$ ,  $M_3(x, y, t) \equiv D_B B(x, y, t) + D_C C(x, y, t) + 2D_E E(x, y, t)$  – diffusion-inhomogeneous complexes. Let us estimate the influence of nonuniform diffusion on the CL according to the experimental data [28,29], according to which at the moments of time  $t = (0, 2, 5, 7, 10)$  at  $T = 50^\circ\text{C}$  the following values of the reagent concentrations  $A \approx (1.00, 0.90, 0.80, 0.75, 0.75)$ ,  $B \approx (1.00, 0.45, 0.30, 0.25, 0.20)$ ,  $C \approx (0.00, 0.15, 0.25, 0.25, 0.30)$ ,  $D \approx (0.00, 0.50, 0.75, 0.80, 0.80)$ ,  $E = (0.00, 0.20, 0.20, 0.30, 0.30)$ . In [29], according to these data for the LMA at i.c.  $[A]_0 = 0.12, [E]_0 = 0$  [mol/l] with an error of  $R_A < 10.4\%$ , the rate constants of the stages were calculated  $k_1 \approx 0.233$ ,  $k_2 \approx 0.535$  [l/(mol×s)], which corresponds to  $k_1 \approx 0.233 \times 0.12 = 0.0280$ ,  $k_2 \approx 0.535 \times 0.12 = 0.0642$ ,  $k_{-1} \approx 0, k_{-2} \approx 0$  [1/s] at  $A_0 = 1, E_0 = 0$ . These constants correspond to low-stage velocities, and non-autonomous CL weakly depends on the kind of kinetic law. Under such

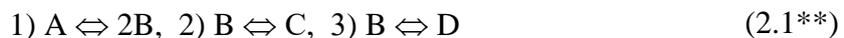
conditions, as noted above, they can be calculated directly from the original equations (1.2) and (1.2\*) (Figure 1).



**Figure 1.** Time dependences of non-autonomous CL with nonuniform diffusion ( $D_A = 0.03$ ;  $D_B = 0.02$ ;  $D_C = 0.01$ ;  $D_D = 0.02$ ;  $D_E = 0.05$ ) for the LMA at  $k_1 = 0.0280$ ,  $k_{-1} = 0$ ,  $k_2 = 0.0642$ ,  $k_{-2} = 0$  at the reactor outlet for mechanisms: (a) (1.1) according to equations (1.2); (b) (1.1\*) according to equations (1.2\*).

Figure 1 (a) it can be seen that for mechanism (1.1)  $K_1 \approx 1$  with an error of less than 5%,  $K_2 = 1$  exactly, and  $K_3 \approx 1$  with an error of about 15%. Figure 1 (b) follows that for mechanism (1.1\*)  $K_1$  deviates from 1 by about 15%,  $K_2 = 1$  exactly, and  $K_3$  deviates from 1 by about 25%. Therefore, taking into account measurement errors, the mechanism (1.1) of the reaction for the production of 4-tert-butylpyrocatechol by oxidation of 4-tert-butylphenol with hydrogen peroxide is in better agreement with all CL and more accurately describes the kinetics of this reaction than mechanism (1.1\*). Note that since the non-autonomous CL  $K_2$  coincides with the corresponding autonomous CL, then, according to the invariant rule, one can conclude the equality of the diffusion coefficients  $D_B \approx D_D$  of the reactants B and D, which form the  $K_2$  complex, and the difference in the diffusion coefficients  $D_B \neq D_C \neq D_A \neq 2D_E$ , which form other complexes.

**Example 2.** Consider a model reaction  $A = C + D$ , which can proceed according to three alternative mechanisms, including independent stages and the same reagents



Let us write down model (2)-(3) for the mechanism (2.1) of this reaction in a nonisothermal adiabatic ( $\beta = 0$ ) plate reactor

$$\frac{\partial A}{\partial t} + q(\frac{\partial A}{\partial x} + \frac{\partial A}{\partial y}) = -r_1 + D_A(\frac{\partial^2 A}{\partial x^2} + \frac{\partial^2 A}{\partial y^2}) \quad (2.2)$$

$$\frac{\partial B}{\partial t} + q(\frac{\partial B}{\partial x} + \frac{\partial B}{\partial y}) = r_1 - r_2 + D_B(\frac{\partial^2 B}{\partial x^2} + \frac{\partial^2 B}{\partial y^2})$$

$$\frac{\partial C}{\partial t} + q(\frac{\partial C}{\partial x} + \frac{\partial C}{\partial y}) = r_2 + D_C(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2})$$

$$\frac{\partial D}{\partial t} + q(\frac{\partial D}{\partial x} + \frac{\partial D}{\partial y}) = r_2 + D_D(\frac{\partial^2 D}{\partial x^2} + \frac{\partial^2 D}{\partial y^2})$$

$$\frac{\partial \theta}{\partial t} + q(\frac{\partial \theta}{\partial x} + \frac{\partial \theta}{\partial y}) = Q_1 r_1 + Q_2 r_2 + D_\theta(\frac{\partial^2 \theta}{\partial x^2} + \frac{\partial^2 \theta}{\partial y^2}) \quad (2.3)$$

where  $A$ ,  $B$ ,  $C$  and  $D$  are the concentration of reagents;  $r_1$ ,  $r_2$  – any kinetic functions. From (2.2)-(2.3), taking into account (6)-(11), it follows that in closed ( $q = 0$ ) and open ( $q \neq 0$ ) plate reactors with uniform diffusion and convection (and in their absence), for the mechanism (2.1) two ( $P = 2$ ,  $N = 4 - 2 = 2$ ) autonomous independent concentration CL of the form (8) are fulfilled, which are expressed through the same complexes

$$K_1(x, y, t) \equiv A(x, y, t) + B(x, y, t) + C(x, y, t) = A^0 + B^0 + C^0 \tag{2.4}$$

$$K_2(x, y, t) \equiv C(x, y, t) - D(x, y, t) = C^0 - D^0$$

At  $\beta = 0$  another autonomous temperature CL of the form (9) is performed:

$$L(x, y, t) \equiv Q_1A(x, y, t) - Q_2C(x, y, t) + \theta(x, y, t) = Q_1A^0 - Q_2C^0 + \theta^0 \tag{2.5}$$

Under i.c.  $A_0 = 1, B_0 = 1, C_0 = D_0 = E_0 = 0$  they have different right-hand sides

$$K_1(l, t) \equiv A + B + C = 1, K_2(l, t) \equiv C - D = 0, L(l, t) \equiv Q_1A - Q_2C + \theta = 2 \tag{2.6}$$

In an open ( $q \neq 0$ ) or closed ( $q = 0$ ) plate reactor with nonuniform diffusion and convection, CL become non-autonomous and are described by equations of the form (12)-(13):

$$\partial K_1/\partial t + q(\partial K_1/\partial x + \partial K_1/\partial y) = \partial^2 M_1/\partial x^2 + \partial^2 M_1A/\partial y^2 \tag{2.7}$$

$$\partial K_2/\partial t + q(\partial K_2/\partial x + \partial K_2/\partial y) = \partial^2 M_2/\partial x^2 + \partial^2 M_2A/\partial y^2$$

$$\partial L/\partial t + q(\partial L/\partial x + \partial L/\partial y) = \partial^2 P/\partial x^2 + \partial^2 P/\partial y^2$$

where  $M_1(x, y, t) \equiv D_{AA}(x, y, t) + D_{BB}(x, y, t) + D_{CC}(x, y, t)$ ,  $M_2(x, y, t) \equiv D_{CC}(x, y, t) - D_{DD}(x, y, t)$ ,  $P(x, y, t) \equiv Q_1D_{AA}(x, y, t) - Q_2D_{CC}(x, y, t) + D_0\theta(x, y, t)$  - diffusion-inhomogeneous complexes.

For the second mechanism (2.1\*), equations (2)-(3) take the form

$$\partial A/\partial t + q(\partial A/\partial x + \partial A/\partial y) = -r_1 + D_A(\partial^2 A/\partial x^2 + \partial^2 A/\partial y^2) \tag{2.2*}$$

$$\partial B/\partial t + q(\partial B/\partial x + \partial B/\partial y) = r_1 - r_2 + D_B(\partial^2 B/\partial x^2 + \partial^2 B/\partial y^2)$$

$$\partial C/\partial t + q(\partial C/\partial x + \partial C/\partial y) = r_1 + D_C(\partial^2 C/\partial x^2 + \partial^2 C/\partial y^2)$$

$$\partial D/\partial t + q(\partial D/\partial x + \partial D/\partial y) = r_2 + D_D(\partial^2 D/\partial x^2 + \partial^2 D/\partial y^2)$$

$$\partial \theta/\partial t + q(\partial \theta/\partial x + \partial \theta/\partial y) = Q_1r_1 + Q_2r_2 + D_\theta(\partial^2 \theta/\partial x^2 + \partial^2 \theta/\partial y^2) \tag{2.3*}$$

Let us write down independent autonomous CL of the form (8)-(9):

$$K_1(x, y, t) \equiv A(x, y, t) + B(x, y, t) + D(x, y, t) = A^0 + B^0 + D^0 \tag{2.4*}$$

$$K_2(x, y, t) \equiv C(x, y, t) + A(x, y, t) = C^0 + A^0$$

$$L(x, y, t) \equiv Q_1A(x, y, t) - Q_2D(x, y, t) + \theta(x, y, t) = Q_1A^0 - Q_2D^0 + \theta^0 \tag{2.5*}$$

These equalities with the same i.c.  $A_0 = 1, B_0 = C_0 = D_0 = 0, \theta_0 = 1$  are written

$$K_1(x, y, t) \equiv A+B+D = 1, K_2(x, y, t) \equiv C+A = 1, L(x, y, t) \equiv Q_1A-Q_2D+\theta = 2 \tag{2.6*}$$

In an open ( $q \neq 0$ ) reactor with nonuniform diffusion and convection, these autonomous CL are violated and are found from equations of the form (12)-(13):

$$\partial K_1/\partial t + q(\partial K_1/\partial x + \partial K_1/\partial y) = \partial^2 M_1^*/\partial x^2 + \partial^2 M_1^*A/\partial y^2 \tag{2.7*}$$

$$\partial K_2/\partial t + q(\partial K_2/\partial x + \partial K_2/\partial y) = \partial^2 M_2^*/\partial x^2 + \partial^2 M_2^*A/\partial y^2$$

$$\partial L/\partial t + q(\partial L/\partial x + \partial L/\partial y) = \partial^2 P^*/\partial x^2 + \partial^2 P^*/\partial y^2$$

where  $M_1^*(x, y, t) \equiv D_{AA}(x, y, t) + D_{BB}(x, y, t) + D_{DD}(x, y, t)$ ,  $M_2^*(x, y, t) \equiv D_{CC}(x, y, t) + D_{AA}(x, y, t)$ ,  $P^*(x, y, t) \equiv Q_1D_{AA}(x, y, t) - Q_2D_{DD}(x, y, t) + D_0\theta(x, y, t)$

For the third mechanism (2.1\*\*), equations (2)-(3) will be written

$$\partial A/\partial t + q(\partial A/\partial x + \partial A/\partial y) = -r_1 + D_A(\partial^2 A/\partial x^2 + \partial^2 A/\partial y^2) \tag{2.2**}$$

$$\partial B/\partial t + q(\partial B/\partial x + \partial B/\partial y) = 2r_1 - r_2 - r_3 + D_B(\partial^2 B/\partial x^2 + \partial^2 B/\partial y^2)$$

$$\begin{aligned} \partial C/\partial t + q(\partial C/\partial x + \partial C/\partial y) &= r_2 + D_C(\partial^2 C/\partial x^2 + \partial^2 C/\partial y^2) \\ \partial D/\partial t + q(\partial D/\partial x + \partial D/\partial y) &= r_3 + D_D(\partial^2 D/\partial x^2 + \partial^2 D/\partial y^2) \\ \partial \theta/\partial t + q(\partial \theta/\partial x + \partial \theta/\partial y) &= Q_1 r_1 + Q_2 r_2 + Q_3 r_3 + D_\theta(\partial^2 \theta/\partial x^2 + \partial^2 \theta/\partial y^2) \end{aligned} \quad (2.3^{**})$$

For this mechanism, there is only one ( $P = 3, N = 4 - 3 = 1$ ) independent autonomous concentration CL of the form (8) and one independent temperature CL of the form (9):

$$K(x, y, t) \equiv 2A(x, y, t) B(x, y, t) C(x, y, t) D(x, y, t) = 2A^0 + B^0 + C^0 + D^0 \quad (2.4^{**})$$

$$L(x, y, t) \equiv Q_1 A(x, y, t) - Q_2 C(x, y, t) - Q_3 D(x, y, t) + \theta(x, y, t) = Q_1 A^0 - Q_2 C^0 - Q_3 D^0 + \theta^0 \quad (2.5^{**})$$

These equalities with the same i.c.  $A_0 = 1, B_0 = C_0 = D_0 = 0, \theta_0 = 1$  are written

$$K(x, y, t) \equiv 2A + B + C + D = 2, L(x, y, t) \equiv Q_1 A - Q_2 C - Q_3 D + \theta = 2 \quad (2.6^{**})$$

In an open ( $q \neq 0$ ) or closed ( $q = 0$ ) plate reactor with nonuniform diffusion and convection, these autonomous CL are violated and are found from equations of the form (12)-(13):

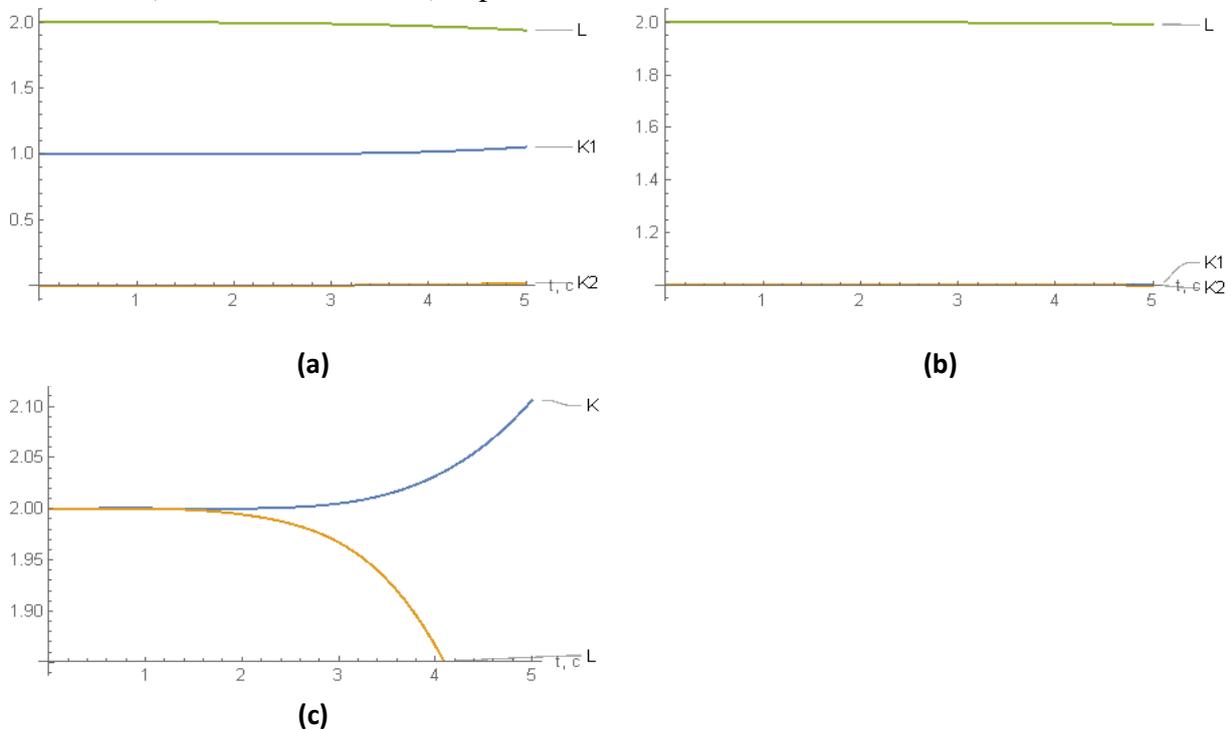
$$\partial K/\partial t + q(\partial K/\partial x + \partial K/\partial y) = \partial^2 M^{**}/\partial x^2 + \partial^2 M^{**}A/\partial y^2 \quad (2.7^{**})$$

$$\partial L/\partial t + q(\partial L/\partial x + \partial L/\partial y) = \partial^2 P^{**}/\partial x^2 + \partial^2 P^{**}/\partial y^2$$

where  $M^{**}(x, y, t) \equiv 2D_A A(x, y, t) + D_B B(x, y, t) + D_C C(x, y, t) + D_D D(x, y, t)$ ,

$P^{**}(x, y, t) \equiv Q_1 D_A A(x, y, t) - Q_2 D_C C(x, y, t) - Q_3 D_D D(x, y, t) + D_\theta \theta(x, y, t)$

It can be seen from the obtained relationships that alternative mechanisms of the  $A = C + D$  reaction, which includes only independent stages with the participation of the same reagents, are characterized by different sets of CL. Let us compare their theoretical values with the model (in the absence of real) experimental data obtained with an unknown kinetic law.



**Figure 2.** Time dependences of non-autonomous CL with nonuniform diffusion ( $D_A = 0.1; D_B = 0.2; D_C = 0.3; D_D = 0.3; D_E = 0.2$ ) for the LMA at  $k_1 = 0.01; k_{-1} = 0.02; k_2 = 0.03; k_{-2} = 0.04; k_3 = 0.05; k_{-3} = 0.06$  и  $q = 0.1, Q_1 = 1, Q_2 = 2, Q_3 = 3$  at the reactor outlet for the mechanisms: **a** - (2.1) according to equations (2.2)-(2.3); **b** - (2.1\*) according to equations (2.2\*)-(2.3\*); **c** - (2.1\*\*) by equations (2.2\*\*)-(2.3\*\*).

Let at the moments of time  $t = (0, 3, 5)$  the concentrations of the reagents are measured at the reactor outlet  $A \approx (1.00, 0.95, 0.90)$ ,  $B \approx (0.00, 0.05, 0.10)$ ,  $C \approx (0.00, 0.05, 0.05)$ ,  $D \approx (0.00, 0.05, 0.05)$  and temperatures  $\theta \approx (1.00, 1.10, 1.05)$  with an error of 5%. Let us first substitute these values into expressions for autonomous CL of different mechanisms. For mechanism (2.1) from (2.7), we find  $K_1 = (1.00, 1.05, 1.05)$ ,  $K_2 = (0.00, 0.00, 0.00)$ ,  $L = (2.00, 1.95, 1.85)$  and the average deviation is  $(5 + 0 + 7.5)/3 \approx 4.66\%$ . For the mechanism (2.1\*) from (2.7\*), we find  $K_1 = (1.00, 1.05, 1.05)$ ,  $K_2 = (1.00, 1.00, 0.95)$ ,  $L = (2.00, 1.95, 1.85)$  and the average deviation is  $(5 + 5 + 7.5)/3 \approx 5.66\%$ . For the mechanism (2.1\*\*) from (2.7\*\*) we find  $K = (2.00, 2.05, 2.00)$ ,  $L = (2.00, 1.80, 1.70)$ , and the average deviation  $(2.5 + 15)/2 \approx 8.75\%$ . Consequently, for autonomous CL, the mechanism (2.1) better agrees with experimental data. Let us further calculate the non-autonomous CL by solving the initial equations at a low stage rate (Figure 2).

Let us compare non-autonomous CL with the corresponding autonomous CL. Figure 2 (a), it can be seen that for mechanism (2.1), the non-autonomous CL  $K_1 \approx 1$ ,  $K_2 \approx 0$  and  $L \approx 2$  deviate from the autonomous ones by less than 5%. Figure 2 (b) it follows that for mechanism (2.1\*), the non-autonomous  $K_1 \approx K_2 \approx 1$  and  $L \approx 2$  deviate from the autonomous also ones by less than 5%. Figure 2 (c) it can be seen that for the mechanism (2.1\*\*), the non-autonomous CL  $K \neq 2$  and  $L \neq 2$  deviate from the corresponding autonomous CL by more than 10%. Consequently, for non-autonomous CL, the mechanisms (2.1) and (2.1\*) of the reaction  $A = C + D$  agree equally well with the experimental data. Thus, based on verifying autonomous and non-autonomous CL, we can assume that mechanism (2.1) is more likely for this reaction. In addition, taking into account that the non-autonomous CL  $K_2$  coincides with the corresponding autonomous CL, according to the invariant rule, one can draw conclusions about the equality of the diffusion coefficients  $D_C \approx D_D$  of the reactants C and D that form this complex, and the difference in the diffusion and convection coefficients that form other complexes.

#### 4. Conclusions

The evolution of concentration and concentration-temperature conservation laws for chemical reactions proceeding unsteadily in a nonisothermal plate reactor with two-dimensional diffusion of reagents and heat convection is investigated. Relationships are found for determining autonomous (uniformly distributed in time and space of the reactor) and non-autonomous (non-uniformly distributed) conservation laws under different assumptions about diffusion and convection. It is shown that these laws depend on the stoichiometry of the reaction stages and the relationship between the intensities of diffusion of reagents and the convection of heat. With a uniform intensity of diffusion and convection, they are autonomous and do not depend on the form of the kinetic law of stages, but with an uneven intensity of diffusion and convection, they become non-autonomous. It was found that different mechanisms of the same reaction, consisting of independent stages, are characterized by different conservation laws. This makes it possible to identify the mechanisms of such reactions from experimental data by measuring concentrations and temperatures at different times in any cross-sections of the reactor. Such measurements also make it possible to identify reagents with close values of the diffusion coefficients. Thus, the established conservation laws can be considered as a kind of "imprints" of the detailed reaction mechanism, which can be used to solve the inverse problem of nonstationary chemical kinetics by choosing the most probable reaction mechanism even with an unknown kinetic law (including a nonideal one).

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## Conflicts of Interest

The authors declared no potential conflict of interest.

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