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Nonequilibrium thermodynamics of autowave processes in a catalyst bed

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Contents

Abstract. A new description of the nature of autowave processes in a static catalyst bed is reviewed by analyzing two kinds of autowaves, fast and slow heat waves. The thermodynamic description of physico-chemical processes is considered and the entropy balance equation is constructed and analyzed taking the quasi-homogeneous (basic) model of an immobile catalyst bed as an approximation. For slow heat waves, the extremal autowave solution functional (total entropy production in the system) is found and a variational formulation of the problem is given. A space – time dissipative structure (a fast heat wave) is shown to exist near the system's thermodynamic equilibrium.

1. Introduction

Autowave processes (AWPs) have been the focus of attention of physicists, mathematicians, chemists, and biologists for a few decades [1 – 24]. Considerable progress in the understanding of autowave properties greatly stimulates interest in nonlinear reaction – diffusion systems that exhibit a large variety of dynamic behaviors and forms of self-organization (see, e.g., Refs [11 – 19] published in *Uspekhi Fizicheskikh Nauk*). The term AWP usually means a self-sustained nonlinear wave process (including stationary structures) whose characteristics (propagation velocity, period, wave (impulse) length, amplitude, and shape) remain unaltered due to an energy source distributed in the medium. In an established regime, these characteristics depend on the local properties of the medium alone and are independent of the initial conditions. Physical media with an energy source at each spatial point are referred to as active media. The energy source can be represented not only by chemical processes but also by processes of a different nature.

Mathematical models of active media that describe various processes in physical [8, 14 – 17, 25, 26], chemical [3, 7, 27 – 31], biological [4, 5, 10, 13, 18, 19, 32 – 39], and other milieu involve the same class of equations. These kinetic equations, which take component transfer processes and their interactions into account, are essentially nonlinear parabolic equations. They are significantly different from hyperbolic equations that describe classical wave systems, including nonlinear ones [3, 13]. We note that real systems always contain some inhomogeneities. Interesting aspects of the nonlinear wave theory related to the effects of autowave localization on medium inhomogeneities are reviewed in Ref. [11].

The theory of nonlinear wave propagation in active extended kinetic systems has its origin in the works of A N Kolmogorov, I G Petrovskiĭ, M S Piskunov [32], R Fisher [33], Ya B Zel'dovich and D A Frank-Kamenetskiĭ [40 – 43]. Today, the mathematical theory of combustion continues to make an important contribution to AWP science (see, e.g., Refs [44 – 49]).

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The phenomenon of heat wave propagation in a static catalyst bed provides a vivid example of AWPs in active heterogeneous systems [50 – 71]. It was first discovered by Frank-Kamenetskii in 1947 and was described as 'migration' of the reaction zone of isopropyl alcohol oxidation over the static bed of a copper catalyst [72]. The object of the study was a porous medium (e.g., an immobile granular layer) through which the reaction mixture was filtered and whose surface was the site of an exothermal catalytic reaction. Characteristic features of this class of systems include filtration of a gas that plays the role of a reactant and heat carrier; high heat capacity of the solid phase compared with that of the gaseous phase; poor effective diffusion of the reactants relative to the effective heat conduction of the layer; and some other properties. Analogs of AWPs in the catalyst static bed have also been found in the processes such as filtering combustion of gases [73 – 87], simultaneous heterogeneous catalysis and homogeneous combustion (hybrid wave) [88], gasless combustion of condensed media and self-propagating high-temperature synthesis [12, 21, 48, 89 – 101], heterogeneous catalytic reaction on a catalyst filament [102 – 107], adsorption [108, 109], and polymerization [110]. Examples of AWPs in nonlinear systems in the absence of a chemical reaction include rearrangement of nucleate and film boiling regimes [111] and propagation of heat waves along an iron wire with the barretter effect [112]. Mathematical models of these systems have much in common despite certain important differences. It is worthwhile to note that the ability of an active extended system to pass from a homogeneous state to a regular heterogeneous state is usually associated with fluctuation rearrangement [113, 114]. From a different standpoint, dissipative structures are formed due to a dynamic rather than fluctuation rearrangement of their state [8].

The principal goals of the AWP theory are elucidation of the general ideas, methodology, and rules pertinent to self-organization processes in various systems and the establishment of the physical magnitude of and criteria for the relative degree of regularity and organization of various nonequilibrium states in open systems. The modern qualitative AWP theory is wholly based on the qualitative theory of dynamic systems [115 – 117]. Successful investigations into nonlinear wave phenomena have greatly promoted the understanding of many of these phenomena based on a common approach and developing a number of universal methods for their survey. In certain particular cases, exact autowave solutions ('traveling waves') of polynomial models [18] and even exact nonstationary solutions of the simplest chain flame propagation model [118] have been obtained.

General laws and causes of self-organization in various systems are considered in the thermodynamics of nonequilibrium processes (nonequilibrium thermodynamics) [113, 114, 119 – 130]. It has been shown that the capacity for self-organization is a common property of open systems and that their regularity is underlain by nonequilibration. The most distinctive examples of self-organization are the Rayleigh – Benard periodic structures in hydrodynamics [131], the Turing patterns [34], and the Belousov – Zhabotinsky reaction [27, 28]. Entropy production may serve as a criterion for the regularity of open systems [132].

We recall that the 'principle of minimum dissipation of energy' introduced by Lord Rayleigh was interpreted by L Onsager in his well-known work on reciprocal relations in irreversible processes. The same author suggested that 'the total rate of increase of the entropy plays the role of a potential'. The general formulation of this principle and demonstration of its importance for linear nonequilibrium steady-state systems were offered by I Prigogine [134]. To date, no general proof of the principle of minimum entropy production in self-organization processes is available for nonlinear systems [132]. At the same time, there are examples of breaches of this principle [135]. The variational problem of phenomenological thermodynamics of reversible processes has been treated in a wealth of publications (see, e.g., [136 – 158]). Analysis of the extremal principles of Onsager, Prigogine, Ziegler, Biot, and Gyarmati is presented in the papers by I P Vyrodov [159, 160]. Thermodynamic systems described by nonlinear kinetic equations were also considered in Refs [134, 161 – 164]. One of the most intriguing problems is the relationship between dynamics and thermodynamics [121, 165]. There are examples of the successful application of methods of nonequilibrium thermodynamics in chemistry and chemical technology [166 – 168]. Naturally, in a single publication, it is impossible to cover the entire range of aspects pertaining to nonequilibrium thermodynamics and its applications.

The above overview demonstrates that principles of self-organization constitute one of the central problems in both nonequilibrium thermodynamics and the AWP theory; therefore, it has become necessary to combine the methods of this theory and nonequilibrium thermodynamics. By way of example, Ref. [169] discusses whether the principle of minimum entropy production can be used to find an autowave solution of the classical problem in the Zel'dovich – Frank-Kamenetskiĭ combustion theory. A positive answer to this question was given in Refs [170 – 172] only after the methodology of nonequilibrium thermodynamics and the AWP theory had been coordinated and validated using a simpler quasi-homogeneous model of a static catalyst bed [173 – 176]. This simplest model of a nonlinear reaction – diffusion system is also a basic model in the context of nonequilibrium thermodynamics. In addition to a thermodynamically reversible process of gas filtration, it takes two irreversible processes into consideration: heat conduction described by the linear Fourier law and chemical reactions described by the nonlinear Arrhenius law.

Along with this line of research, a direct method for integration of nonlinear reaction – diffusion equations has been developed [177] based on the dynamic minimum dissipation principle [178, 179]. Reference [177] gives examples of its application for estimating steady velocities of autowaves. Specifically, the propagation velocity of laminar combustion autowaves was estimated in the approximation of a narrow reaction zone; it turned out to coincide with that found from the classic Zel'dovich – Frank-Kamenetskiĭ formula. We note that mechanical analogs of basic postulates of nonequilibrium thermodynamics were formulated in the works of I F Bakhareva [142, 143].

The acquisition of ideas of nonequilibrium thermodynamics by the AWP theory has been promoted by the discovery of the propagation of fast heat waves (FHWs) [67 – 70]. This phenomenon is feasible only when a reversible chemical reaction proceeds in a static catalyst bed, with the reaction mixture passing from one state of thermodynamic equilibrium to another. The existence of FHWs (first-type automodel solutions) is rigorously derived from the analysis of a quasi-homogeneous model. FHWs are essentially different from the well-known slow heat waves (SHWs), i.e., second-type automodel solutions, in which the reaction

mixture passes from a low-temperature metastable state at the input of the catalyst bed to thermodynamic equilibrium at high temperatures. According to the nonlinear law formulated by Arrhenius for the chemical reaction rate, FHWs are likely to arise both far from and close to thermodynamic equilibrium [69, 70]. It is noteworthy that the existence of FHWs became known when processes resulting in their formation had already proceeded in large-capacity industrial reactors (see references in [66, 180]).

The present review is concerned with a quasi-homogeneous model of the static catalyst bed that allows the nature of autowave phenomena to be elucidated. Two types of autowaves, FHWs and SHWs, are considered. Methods and approaches employed in AWP studies are discussed. Much attention is given to the nonequilibrium thermodynamics of AWPs, which facilitates the understanding of the causes and driving forces of self-organization. The principle of minimum total entropy production in AWPs is established and a variational formulation of the SHW propagation problem is proposed.

The contents of the subsequent sections of the review are briefly as follows. Section 2 deals with traditional problems of mathematical simulation of AWPs. A basic model of AWPs in a static catalyst bed is given for a reversible chemical reaction proceeding by a simple mechanism and the behavior of phase trajectories of the system is investigated. Conditions necessary for FHWs and SHWs to exist are discussed. Section 3 is focused on the central issue of the review, the development of a thermodynamic theory of AWPs. This section describes derivation of the entropy balance equation in the approximation of a quasi-homogeneous (basic) model of the static catalyst bed. Also presented is the analysis of the contribution of physico-chemical processes to the local and total entropy production in the system. Section 4 illustrates application of methods and approaches of nonequilibrium thermodynamics to the problem of SHW propagation during sulfur dioxide oxidation. The last section concludes the review.

2. Autowave solutions for the quasi-homogeneous model of a static catalyst bed

2.1 Mathematical model of nonstationary processes in a static catalyst bed

The static catalyst bed is a complex system with the inevitable statistical distribution of properties in individual structural elements. The complexity of the system is increased by a nonuniform dispersion of the heterogeneous medium, turbulence of the flows, and other factors. Equations of mathematical physics constitute a theoretical basis, a prototype, for the development and optimization of catalytic processes, but their macroscopic parameters, unlike those of classical equations of mathematical physics for continuous media, play the role of effective quantities. Mathematical models of the static catalyst bed in the general form are rather complicated. A number of specific requirements are imposed for the construction, selection, and simplification of such models [181].

We consider a simple (quasi-homogeneous) model. Such a model takes into account a convective flow of the gaseous reaction mixture through the static catalyst bed, the effective heat conduction of the blown-through granular layer, and the chemical transformation that serves as a source of heat and matter. The processes of heat and mass transfer in a catalyst granule are supposed to be so intense that the difference in temperature and concentration between the gas and the catalyst may be neglected. Here, we consider a gas flow with a negligibly small pressure gradient under the assumption that the reaction mixture satisfies the ideal gas law. Such a highly formalized representation of the complex system makes its mathematical model, capturing the principal characteristics of the phenomenon under study, suitable for qualitative and numerical analysis.

When a single reaction proceeds in the catalyst bed, the one-dimensional quantity balance equation for the kth component in the porous medium approximation (as two interpenetrating continua) has the form

$$\varepsilon_{\mathrm{g}} \frac{\partial \rho_k}{\partial t} = -\frac{\partial(\rho_k u_k)}{\partial \ell} + \chi_k M_k v(T, p_k)\,, \qquad k = 1, \ldots, n\,. \quad (1)$$

Here, ρ_k and p_k are the respective density and partial pressure of the kth component; u_k is the velocity of the kth component through the total cross section of the catalyst bed; χ_k is the stoichiometric coefficient at the kth component involved in the chemical reaction; M_k is the molecular weight of the kth component; v is the chemical reaction rate (mol m^{-3} s^{-1}); t is the time; ℓ is the longitudinal coordinate; $\varepsilon_{\mathrm{g}} = \varepsilon + (1-\varepsilon)\varepsilon_{\mathrm{p}}$ is the volume fraction of the gaseous phase; and ε and ε_{p} are the porosity of the catalyst bed and granule.

Summing (1) over all components, we obtain the mass conservation equation

$$\varepsilon_{\mathrm{g}} \frac{\partial \rho_{\mathrm{g}}}{\partial t} = -\frac{\partial(\rho_{\mathrm{g}} u)}{\partial \ell}\,, \quad (2)$$

where we used that

$$\sum_{k=1}^{n} \chi_k M_k = 0\,.$$

Here,

$$\rho_{\mathrm{g}} = \sum_{k=1}^{n} \rho_k\,;$$

and

$$u = \frac{1}{\rho_{\mathrm{g}}} \sum_{k=1}^{n} \rho_k u_k$$

is the mass-averaged velocity of the flow per total cross section of the catalyst bed.

It is known that the stoichiometric equation for any chemical reaction may be used to calculate changes in the number of moles of all its components from those of the key component [182, 183]. The fundamental laws of thorough equilibrium imply that the chemical reaction rate must take the reversible character of chemical transformations into account [182–187],

$$v = v_+ - v_- = v_+ \left[1 - \frac{v_-}{v_+}\right],$$

where v_+ and v_- are the respective velocities of forward and backward reactions.

We note that from the standpoint of kinetic reversibility, all reactions can be categorized into reversible, i.e., proceed-

ing simultaneously in the direct and reverse directions, and irreversible, i.e., proceeding only in either of the two directions until at least one reagent is ultimately exhausted. For this reason, the reversibility term (in square brackets) is dropped in the calculation of the material balance for kinetically irreversible reactions. It must be emphasized that such a simplification is not always justified. In using methods of nonequilibrium thermodynamics, it seems expedient to take reversibility of chemical transformations into consideration because in the case where the reaction equilibrium constant is chosen properly but no additional assumptions are introduced, the results are practically the same as in the case where the reversibility is not taken into account. Moreover, the presence of the reversibility term in a kinetic model may help to obviate difficulties encountered in the investigation of reactions involving different orders because characteristics of a singular point of the system of equations at high temperatures are strongly dependent on the form of the kinetic mode.

For simplicity, we consider a reversible chemical reaction $A \rightleftarrows B$ whose velocity is described by the expression [184–186]

$$v = k_0 \exp\left(-\frac{E}{RT}\right) C_A \left[1 - \frac{p_B}{p_A K_p(T)}\right] = k_0 C_0 \exp\left(-\frac{E}{RT}\right) C \left[1 - \frac{1-C}{C K_p(T)}\right], \quad (3)$$

where k_0 is the pre-exponential factor of the reaction rate constant, E is the activation energy of the reaction, R is the universal gas constant, C_A is the concentration of reagent A, p_A and p_B denote partial pressure of reagents A and B, respectively,

$$K_p(T) = \exp\left(-\frac{\Delta G_T^0}{RT}\right) = \exp\left(-\frac{\Delta H_T^0}{RT} + \frac{\Delta S_T^0}{R}\right) = k_e \exp\left(\frac{q}{RT}\right)$$

is the equilibrium constant of the reaction, ΔG_T^0, ΔH_T^0, and ΔS_T^0 are the respective Gibbs energy, enthalpy, and entropy of the reaction at standard pressure, k_e is the pre-exponential factor of the reaction rate constant, $C = C_A/C_0$ is the dimensionless concentration (mass fraction) of reagent A, $C_0 = C_A + C_B$ is the total concentration of reactants in the reaction mixture, $q = -\Delta H_T^0$ is the thermal effect of the reaction, and $p_k = C_k RT$.

The hypothesis of local thermodynamic equilibrium permits us to introduce the specific enthalpy of the gas h_g and the catalyst h_c, temperature T, pressure p, and other thermodynamic functions.

Based on the general notions of density, current, and source of a substance, we introduce functions of the enthalpy density of the gas $\rho_g h_g$ and the catalyst $\rho_c h_c$, and the convective $\rho_g u h_g$ and conductive J_q flow of enthalpy. All these variables are related by the enthalpy balance equation

$$\frac{\partial(\varepsilon_g \rho_g h_g + \varepsilon_c \rho_c h_c)}{\partial t} = -\frac{\partial(\rho_g u h_g)}{\partial \ell} - \frac{\partial J_q}{\partial \ell}, \quad (4)$$

where $h_g = (\rho_A h_A + \rho_B h_B)/\rho_g$, $h_A(T) = h_A^0 + c_p(T - T_0)$ and $h_B(T) = h_B^0 + c_p(T - T_0)$ are partial enthalpies of reagents A and B per unit mass, ρ_A and ρ_B are the densities of reagents A and B, $\varepsilon_c = 1 - \varepsilon_g$ is the catalyst volume fraction, and c_p is the heat capacity of the gas.

A change in enthalpy in Eqn (4) is due to the changes of the observed system parameters such as temperature, pressure, densities, and concentrations of its components.

If cross diffusion of the components is neglected in Eqn (4), the conductive enthalpy flow becomes a heat flow proper, described with a good degree of accuracy by the linear Fourier law of heat conduction ($J_q = -\lambda \operatorname{grad} T$). Taking continuity equation (2) into account, assuming the effective heat conduction coefficient of the catalyst bed and specific heat capacities of the gaseous and solid phases (per unit mass) to be constant, and using the apparatus of partial thermodynamic functions [182], it can be shown that Eqn (4) is equivalent to

$$(\varepsilon_g \rho_g c_p + \varepsilon_c \rho_c c_c) \frac{\partial T}{\partial t} = \lambda \frac{\partial^2 T}{\partial \ell^2} - \rho_g u c_p \frac{\partial T}{\partial \ell} + q C_0 k_0 \exp\left(-\frac{E}{RT}\right) C \left[1 - \frac{1-C}{C K_p(T)}\right], \quad (5)$$

where c_c is the catalyst heat capacity and $\mathrm{d}h_c = c_c \,\mathrm{d}T$. Thus, we have arrived at the known equation of convective diffusion with a source.

We reduce material balance equation (1) for reagent A, taking (2) into account, to the form

$$\varepsilon_g \frac{\partial C}{\partial t} = -u \frac{\partial C}{\partial \ell} - k_0 \exp\left(-\frac{E}{RT}\right) C \left[1 - \frac{1-C}{C K_p(T)}\right]. \quad (6)$$

The system of equations (5), (6) is considered with the following boundary and initial conditions:

$$\ell = \frac{-L}{2}: \quad \lambda \frac{\partial T}{\partial \ell} = \rho_g u c_p (T - T_0), \qquad C = \frac{C_{A,0}}{C_0}, \quad (7)$$

$$\ell = \frac{+L}{2}: \quad \lambda \frac{\partial T}{\partial \ell} = 0, \quad (8)$$

$$t = 0: \qquad T(0, \ell) = T_n, \qquad C(0, \ell) = C_n. \quad (9)$$

Here, L is the length of the catalyst bed, T_0 is the temperature at the input of the catalyst bed, $C_{A,0}$ is the concentration of reagent A at the input of the catalyst bed, T_n is the initial temperature of the bed, and C_n is the dimensionless initial concentration of reagent A.

The mathematical model in (5)–(9) is the simplest one that allows the interpretation of the most important experimentally observed phenomena and regular processes in a static catalyst bed, in particular, heat front formation and propagation [69, 70]. Minimal simplification of the model by neglecting conductive heat transfer leads to an ideal displacement model unfit for the description of heat front propagation.

Before turning to the application of the methods and approaches of the AWP theory, we demonstrate the results of simulating nonstationary processes in a static catalyst bed. The computation was performed using the parameter values

$$C_0 = 46.43 \text{ mol m}^{-3}; \quad c_c = 249 \text{ cal kg}^{-1} \text{ K}^{-1};$$
$$c_p = 300 \text{ cal kg}^{-1} \text{ K}^{-1}; \quad E = 20 \text{ kcal mol}^{-1};$$
$$q = 15 \text{ kcal mol}^{-1}; \quad k_0 = 4.52 \times 10^7 \text{ s}^{-1};$$
$$k_e = 5.737 \times 10^{-5}; \quad u = 1 \text{ m s}^{-1}; \quad \varepsilon = 0.42;$$
$$\varepsilon_p = 0.3; \quad \lambda = 0.2 \text{ cal m}^{-1} \text{ s}^{-1} \text{ K}^{-1};$$
$$\rho_g = 1.3 \text{ kg m}^{-3}; \quad \rho_c = 2700 \text{ kg m}^{-3},$$

where C_0, u, and ρ_g are given at the input conditions.

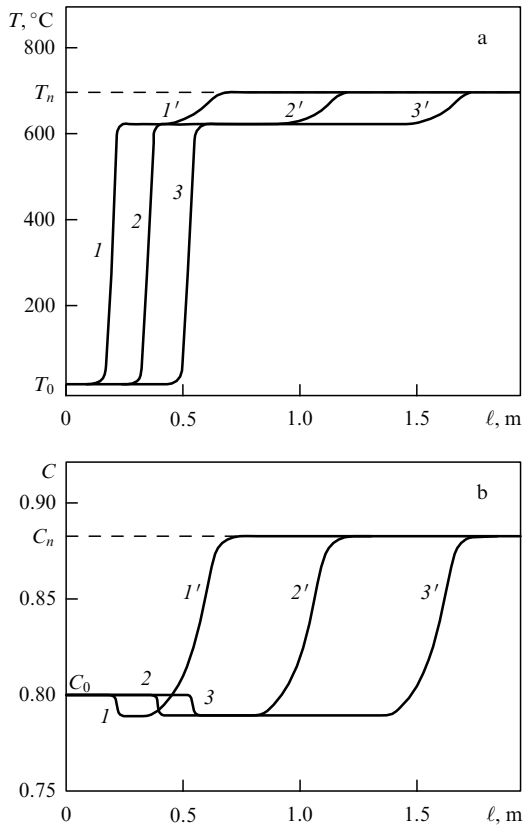

Figure 1. The temperature (a) and reagent A concentration (b) profiles along the catalyst bed at consecutive time moments: curves *1*, *1′* — $t = 120$ s, curves *2*, *2′* — $t = 240$ s, curves *3*, *3′* — $t = 360$ s. The input and initial conditions: $T_0 = 20\,^\circ$C, $C_{A,0} = 34.82$ mol m^{-3}, $T_n = 700\,^\circ$C, and $C_n = 0.8816$.

Figure 1 shows the temperature and reagent A concentration profiles over the catalyst bed at consecutive time moments calculated using model (5)–(9). It can be seen that two reaction zones are formed in the catalyst bed initially heated to the temperature T_n. These zones migrate in the direction of the gas flow with different but constant linear velocities.

In the front zone, the temperature rises from 20 to 620 °C, with the chemical transformation process releasing heat and the reagent A concentration decreasing from the input value to the equilibrium one corresponding to 620 °C. This temperature is higher than the temperature of adiabatic heating of the reaction mixture (superadiabaticity effect) (see, e.g., [65, 79, 80]). Its maximum (thermodynamically equilibrated) value is independent of T_n in a broad range of initial temperature variations and is determined by processes proceeding in the first zone. These processes are peculiar in that the chemical reaction and heat conduction interfere with the cooling of the catalyst bed by a convective gas flow. This accounts for the propagation velocity of the first reaction zone being lower than that of the inert heat label in the catalyst bed.

In the second zone, the temperature rises from 620 °C to T_n, but chemical transformation occurs with heat absorption, unlike that in the first zone. Product B is converted back to the starting reagent A, whose concentration increases from the equilibrium value at 620 °C to an equilibrium value at T_n. The catalyst bed is cooled both by the convective gas flow and due to the endothermal chemical reaction. Therefore, the velocity of the second reaction zone is much higher than that of the inert heat label in the catalyst bed.

Because a stationary heat wave travels over the catalyst bed with a certain constant velocity and retains its spatial structure, it exists (strictly speaking) only when the catalyst bed is infinitely long and asymptotically formed as $t \to \infty$. Of course, it is then necessary that the chemical conversion rate be low in a certain vicinity of the input conditions [65, 68]. Unfortunately, experiment, even a numerical one, is restricted in both space and time. However, specific approaches and asymptotic notions introduced in the theory of combustion afford insights into the nature of autowave propagation without accounting for transient processes.

2.2 Mathematical model of autowave processes

The history of the theory of AWPs in a static catalyst bed is rather short. The first data on the propagation of reaction waves during isopropyl alcohol oxidation in the static bed of a copper catalyst were reported by D A Frank-Kamenetskiĭ [72]. Since then, a considerable number of theoretical and experimental studies have been devoted to this subject (see, e.g., Refs [66, 180]).

Autowave processes in a static catalyst bed are in many aspects similar to heat front propagation processes during filtration of a combustible gas mixture through an inert porous medium [73–87]. In such processes, the gas temperature in the reaction zone is naturally higher than the solid phase temperature. All these processes have many close analogies with laminar combustion processes. But meaningful results from the combustion theory have no direct application because of the very dissimilar nature of the two phenomena [64]. For example, dynamic properties of an immobile granular layer are for the most part determined by markedly different heat capacities of the solid and gaseous phases and by filtration of the reaction mixture.

Investigations into the steady propagation of autowaves are actually restricted to the search for stationary solutions of the system of equations (5), (6) over an infinite interval during sufficiently long times $t \to \infty$. As the catalyst bed is extended to infinity, the characteristics of the relevant process must be preserved: the coefficients in the equations must be kept unchanged and the boundary conditions transferred to infinity. In a sufficiently extended catalyst bed (at large contact times), condition (8) corresponds to the condition of thermodynamic equilibrium in the reaction mixture when both the chemical affinity and the reaction rate vanish [182–186]:

$$A = RT_\infty \ln \frac{K_p(T_\infty)C_\infty}{1 - C_\infty} = 0\,, \qquad v(T_\infty, C_\infty) = 0\,. \tag{10}$$

The thermodynamically equilibrated values of temperature (T_∞) and reactant concentrations (C_∞) are then related by

$$C_\infty = \frac{1}{K_p(T_\infty) + 1}\,. \tag{11}$$

Hence, instead of (8), it is more convenient to use the equivalent equation

$$\ell \to +\infty: \quad T \to T_\infty\,, \quad C \to C_\infty(T_\infty)\,. \tag{12}$$

The solution of problem (5)–(9) in the form of a traveling wave

$$T = T(\ell - V_{\rm f}\,t)\,, \quad C = C(\ell - V_{\rm f}\,t)$$

is to be sought in the class of smooth bounded functions. If such a steady-state solution does exist, problem (5)–(9) in a moving frame of coordinates associated with the propagating front ($\xi = \ell - V_{\rm f}\, t + \text{const}$, $\partial/\partial t = -V_{\rm f}\, {\rm d}/{\rm d}\xi$) is reduced to the following stationary problem [67–71]:

$$\lambda \frac{{\rm d}^2 T}{{\rm d}\xi^2} - \rho_{\rm g} u c_p \left(1 - \gamma \frac{V_{\rm f}}{u}\right) \frac{{\rm d}T}{{\rm d}\xi} + q C_0 k_0 \exp\left(-\frac{E}{RT}\right) C \left[1 - \frac{1-C}{C K_p(T)}\right] = 0\,, \tag{13}$$

$$-u\left(1 - \varepsilon_{\rm g} \frac{V_{\rm f}}{u}\right) \frac{{\rm d}C}{{\rm d}\xi} - k_0 \exp\left(-\frac{E}{RT}\right) C \left[1 - \frac{1-C}{C K_p(T)}\right] = 0\,, \tag{14}$$

$$\xi \to -\infty: \quad \lambda \frac{{\rm d}T}{{\rm d}\xi} - \rho_{\rm g} u c_p (T - T_0) \to 0\,, \quad C \to \frac{C_{\rm A,0}}{C_0}\,, \tag{15}$$

$$\xi \to +\infty: \quad T \to T_\infty\,, \quad C \to C_\infty(T_\infty)\,. \tag{16}$$

Here,

$$\gamma = \varepsilon_{\rm g} + \frac{\varepsilon_{\rm c} \rho_{\rm c} c_{\rm c}}{\rho_{\rm g} c_p}$$

and $V_{\rm f}$ is the unknown parameter determining the front propagation velocity.

In a moving system of coordinates, continuity equation (2) becomes

$$\frac{{\rm d}\big(\rho_{\rm g}(u - \varepsilon_{\rm g} V_{\rm f})\big)}{{\rm d}\xi} = 0\,.$$

With condition (15), this implies that

$$\rho_{\rm g}(u - \varepsilon_{\rm g} V_{\rm f}) = \text{const}\,.$$

Therefore, it is useful to assume that $\rho_{\rm g}$, u, and C_0 are defined at the input conditions.

Passing to the dimensionless variables

$$r = \frac{\xi \rho_{\rm g} u c_p}{\lambda}\,, \qquad z = \frac{C_{\rm A,0} - C_{\rm A}}{C_0}\,, \tag{17}$$

we rewrite problem (13)–(16) as

$$\frac{{\rm d}^2 T}{{\rm d}r^2} - (1-\omega)\frac{{\rm d}T}{{\rm d}r} + T_{\rm ad} K_1(T) \left[z_{\rm A,0} - z - \frac{1 - z_{\rm A,0} + z}{K_p(T)}\right] = 0\,, \tag{18}$$

$$(1 - \alpha\omega)\frac{{\rm d}z}{{\rm d}r} = K_1(T)\left[z_{\rm A,0} - z - \frac{1 - z_{\rm A,0} + z}{K_p(T)}\right], \tag{19}$$

$$r \to -\infty: \quad \frac{{\rm d}T}{{\rm d}r} - (T - T_0) \to 0\,, \quad z \to 0\,, \tag{20}$$

$$r \to +\infty: \quad T \to T_\infty\,, \quad z \to z_{\rm e}(T_\infty)\,, \tag{21}$$

where $\omega = \gamma V_{\rm f}/u$ is the dimensionless propagation velocity of the autowave,

$$T_{\rm ad} = \frac{q C_0}{\rho_{\rm g} c_p}\,, \qquad z_{\rm A,0} = \frac{C_{\rm A,0}}{C_0}\,,$$

$$K_1(T) = \frac{\lambda}{\rho_{\rm g} c_p u^2}\, k_0 \exp\left(-\frac{E}{RT}\right), \qquad \alpha = \frac{\varepsilon_{\rm g}}{\gamma}\,.$$

By substituting (19) in (18), we find a first integral of the system and reduce the order of Eqn (18),

$$\frac{{\rm d}T}{{\rm d}r} = (1-\omega)T - T_{\rm ad}(1 - \alpha\omega)z + N\,, \tag{22}$$

where N is the integration constant.

It follows from Eqn (22) and conditions (20) that

$$\frac{{\rm d}T}{{\rm d}r} = (1-\omega)T - T_{\rm ad}(1 - \alpha\omega)z + N \to T - T_0$$

as $r \to -\infty$. Hence, if $\omega = 0$, then $N = -T_0$ and if $\omega \neq 0$, then

$$\frac{{\rm d}T}{{\rm d}r} = (1-\omega)T + N \to T - T_0$$

as $r \to -\infty$. In other words, the limit of the function and the limit of its derivative exist and are finite; this is possible if $N = -(1-\omega)T_0$.

Thus, the condition at $r \to -\infty$ for T at $\omega \neq 0$ is split into two: the conditions $T \to T_0$ and ${\rm d}T/{\rm d}r \to 0$; that is, problem (18)–(21) is transformed into

$$\frac{{\rm d}T}{{\rm d}r} = (1-\omega)(T - T_0) - T_{\rm ad}(1 - \alpha\omega)z\,, \tag{23}$$

$$\frac{{\rm d}z}{{\rm d}r} = K_2(T)\,\frac{z_{\rm e}(T) - z}{1 - \alpha\omega}\,, \tag{24}$$

$$r \to -\infty: \quad T \to T_0\,, \quad z \to 0\,, \tag{25}$$

$$r \to +\infty: \quad T \to T_\infty\,, \quad z \to z_{\rm e}(T_\infty)\,, \tag{26}$$

where

$$K_2(T) = \frac{K_1(T)\big(1 + K_p(T)\big)}{K_p(T)}$$

and

$$z_{\rm e}(T) = z_{\rm A,0} - \frac{1}{1 + K_p(T)}$$

is the equilibrium degree of transformation corresponding to the temperature T.

To summarize, the mathematical model of autowave processes in a static catalyst bed is the boundary problem (23)–(26) for a system of two ordinary differential equations with parameters ω and T_∞. The currently available methods and approaches for the qualitative analysis of second-order dynamic (autonomous) systems make it possible to study the properties of the solution 'at large' [116, 117]. Eliminating the autonomous (wave) variable r from dynamic system (23), (24) (by division) leads either to the differential equation

$$\frac{{\rm d}z}{{\rm d}T} = \frac{K_2(T)\big[z_{\rm e}(T) - z\big]}{(1 - \alpha\omega)\big[(1-\omega)(T - T_0) - T_{\rm ad}(1 - \alpha\omega)z\big]}\,, \tag{27}$$

or to the differential equation

$$\frac{{\rm d}T}{{\rm d}z} = \frac{\big[(1-\omega)(T - T_0) - T_{\rm ad}(1 - \alpha\omega)z\big](1 - \alpha\omega)}{K_2(T)\big[z_{\rm e}(T) - z\big]}\,. \tag{28}$$

We recall that a dynamic system in a certain domain of the Euclidean plane (with Cartesian coordinates z and T) determines a family of trajectories (division of the domain into trajectories) [116]. In system (23), (24), the trajectories (integral curves) are found with the help of parametric

equations; in Eqns (27) and (28), the trajectories are determined by equations in the Cartesian coordinates.

Equilibrium states (singular points) of a dynamic system on the phase plane (z, T) are defined by the intersection of null isoclines (principal isoclines). The null isocline of Eqn (23) is the straight line

$$z = \frac{(1-\omega)(T-T_0)}{(1-\alpha\omega)T_{\mathrm{ad}}} \,. \tag{29}$$

At points of null isocline (29), tangents to the trajectories are vertical lines (parallel to the z axis). Equation (24) has two null isoclines. One of them is the thermodynamic equilibrium reaction curve $z = z_{\mathrm{e}}(T)$; at its points, tangents to the trajectories are horizontal. It is worth noting that this S-shaped curve is defined only by parameters entering the equilibrium constant. The other null isocline of Eqn (24) is the straight line $T = 0$ K (the axis of the degrees of transformation), where the reaction rate strictly vanishes, in agreement with the Arrhenius law, regardless of reagent concentrations.

Therefore, the singular points of system (23), (24) are given by zeroes T_s of the function

$$f(T) = \frac{(1-\omega)(T-T_0)}{(1-\alpha\omega)T_{\mathrm{ad}}} - z_{\mathrm{e}}(T) \,, \tag{30}$$

and by the intersection of null isocline (29) with the null isocline $T = 0$ K.

We note that the extension of the temperature range to $T_0 = 0$ K is permissible from the mathematical standpoint because problem (23)–(26) is free of constraints in the range of positive temperatures; the singular point of the dynamic system is its most important characteristic.

The equality

$$\frac{(1-\omega)(T_\infty - T_0)}{1-\alpha\omega} = T_{\mathrm{ad}} z_{\mathrm{e}}(T_\infty) \tag{31}$$

expresses the integral energy balance. It establishes a one-to-one correspondence between the parameters ω and T_∞. Hence, problem (23)–(26) contains a single unknown parameter, either ω or T_∞.

Solutions of the system of equations (23), (24) at all r make sense only if they are belong to the physical domain of the phase space (z, T), i.e., for nonnegative dimensional values of reagent concentrations and positive absolute temperatures. There is no chemical transformation at $\omega = 1/\alpha$, and the problem makes no sense. If $\omega > 1/\alpha$, each component of a trajectory originating in the physical domain of the phase space decreases indefinitely as $r \to +\infty$; in other words, it leaves the physical domain of the phase space. At $\omega < 1/\alpha$, if a trajectory originating in the physical domain of the phase space remains inside it as $r \to +\infty$, it converges to the singular point $\big(z_{\mathrm{e}}(T_\infty), T_\infty\big)$. It follows from the above that the admissible range of ω values is defined by the inequality $\omega < 1/\alpha$.

Unlike the position of a thermodynamic equilibrium isocline on the phase plane, the position of null isocline (29) is essentially ω-dependent. For example, the degree of transformation of the starting reagent z at points of null isocline (29) at $\omega < 1$ grows with temperature but decreases at $1 < \omega < 1/\alpha$. At $\omega = 1$, null isocline (29) is a straight line $z = 0$ parallel to the temperature axis. This means that the velocity $\omega = \gamma V_{\mathrm{f}}/u = 1$ equals the propagation velocity of the inert (and simultaneously losing distinctness) heat label. This asymptotic velocity value makes a 'barrier' that separates fast and slow autowaves [67–70]. Although the FHW and SHW propagation velocities may be of the same order, the properties of these waves are substantially different.

Concrete examples of phase portraits with differently positioned null isoclines and phase trajectories of the system of equations (23), (24) connecting singular (stationary) points are considered at greater length in the next sections.

2.3 Necessary conditions for the existence of fast heat waves

In what follows, in order to concentrate attention on the phenomenon of FHW propagation, we assume the equilibrium composition of the reaction mixture at the entry to a catalyst bed, i.e., $z_{\mathrm{A},0} = 1/\big(1 + K_p(T_0)\big)$. Hence, $z_{\mathrm{e}}(T_0) = 0$, $T_0 > 0$ K.

We introduce the dimensionless temperature and parameter

$$\theta = \frac{T - T_0}{\beta T_0} \,, \qquad \beta = \frac{RT_0}{E} \,. \tag{32}$$

Then, problem (23)–(26) takes the form

$$\frac{\mathrm{d}\theta}{\mathrm{d}r} = (1-\omega)\theta - (1-\alpha\omega)Qz \,, \tag{33}$$

$$\frac{\mathrm{d}z}{\mathrm{d}r} = K^0(\theta)\frac{z_{\mathrm{e}}(\theta) - z}{1-\alpha\omega} \,, \tag{34}$$

$$r \to -\infty: \qquad \theta \to 0 \,, \qquad z \to 0 \,, \tag{35}$$

$$r \to +\infty: \qquad \tau \to \theta_\infty \,, \qquad z \to z_{\mathrm{e}}(\theta_\infty) \,. \tag{36}$$

Here,

$$Q = \frac{qC_0}{\rho_{\mathrm{g}} c_p \beta T_0} \,, \qquad K^0(\theta) = \frac{K(\theta)\big(1 + K_p(\theta)\big)}{K_p(\theta)}$$

and

$$z_{\mathrm{e}}(\theta) = z_{\mathrm{A},0} - \frac{1}{1 + K_p(\theta)}$$

is the equilibrium degree of transformation corresponding to the temperature θ; next,

$$K(\theta) = k_r \exp\left(\frac{\theta}{1+\beta\theta}\right), \qquad k_r = \frac{\lambda}{\rho_{\mathrm{g}} c_p u^2} k_0 \exp\left(-\frac{1}{\beta}\right),$$

$$K_p(\theta) = K_{p,0} \exp\left[-\frac{(\eta-1)\theta}{1+\beta\theta}\right],$$

$$K_{p,0} = k_{\mathrm{e}} \exp\left(\frac{\eta - 1}{\beta}\right), \qquad \eta = \frac{E+q}{E} \,.$$

The domain of definition of the dimensionless temperature is $\theta > -1/\beta$.

Equations (33) and (34) reflect the FHW energy and material balance, respectively. It is worth noting that the system of equations (33), (34) has no periodic solution because the Bendixson criterion is satisfied [116]. The singular points $(\theta_{\mathrm{s}}, z_{\mathrm{s}})$ of the system on the phase plane (θ, z) are defined by the intersection of null isoclines. One of them is the thermodynamic equilibrium curve of the reaction $z = z_{\mathrm{e}}(\theta)$ and the other (straight line) is the heat balance null

isocline

$$z = \frac{(1-\omega)\theta}{(1-\alpha\omega)Q}\,. \tag{37}$$

Furthermore, the singular points are defined by zeroes θ_s of the function

$$f(\theta) = \frac{(1-\omega)\theta}{1-\alpha\omega} - Qz_e(\theta)\,. \tag{38}$$

The integral energy balance (31) becomes

$$\omega = \frac{\theta_\infty - Qz_e(\theta_\infty)}{\theta_\infty - \alpha Q z_e(\theta_\infty)}\,. \tag{39}$$

The value of θ_∞ equals the initial temperature of a catalyst bed of constant length. Then, Eqn (39) unambiguously defines ω. By setting $\theta_\infty > -1/\beta$, it is possible to find a value of ω at which the point $(z_e(\theta_\infty), \theta_\infty)$ is singular for system of equations (33), (34). It follows from the position of the null isocline on the phase plane that $1 < \omega < 1/\alpha$ in this case.

The thermodynamic equilibrium curve $z = z_e(\theta)$ in Fig. 2 has an inflection point denoted as *I*. Let the point $(0,0)$ coincide with the inflection point *I*. Then, at an arbitrary θ_∞, it is a saddle point, and null isoclines intersect thrice if $f(-1/\beta) > 0$ and twice if $f(-1/\beta) < 0$. In the former case, one stable node is located to the right and the other to the left of *I*. In the latter case, the stable node is on the right from the origin. Accordingly, there are two (or one) separatrixes that connect the stable node with the saddle singular point. These separatrixes are the FHW images on the phase plane (z, θ). When there are two separatrixes, they correspond to a single ω value. If $(0,0)$ does not coincide with *I*, it may be either a saddle or a node depending on the value of θ_∞.

Unfortunately, in the framework of this review, we cannot give the complete exposition of the relation between all parameters of system (33), (34) and the FHW characteristics. In what follows, only selected examples are considered. The results obtained can be summarized as lemmas and corollaries in the Appendix.

The condition $f'(\theta_s) > 0$ may be represented, using (38), as

$$\frac{z_e(\theta_\infty)}{\theta_\infty} > z_e'(\theta_s)\,. \tag{40}$$

For $\theta_s = 0$, this means that the origin $(0,0)$ is a saddle singular point if the tilt of the tangent to the thermodynamic equilibrium curve at this point is smaller than that of the second null isocline connecting $(0,0)$ with the other singular point. Otherwise, the origin is a stable node.

We consider the case where the inflection point lies to the left of $(0,0)$ (see Fig. 2). Let the tangent to curve *1* at the origin cross it at $\theta = \theta_{cr}$. Then, for the values $\theta_\infty \in (\theta_{cr}, 0)$, the point $(0,0)$ is a stable node because condition (40) is violated and the null isoclines intersect at three points, of which the middle one is a saddle. Hence, problem (33)–(36) has no solution at θ_∞, and the regime of FHW propagation over the catalyst bed is impossible. It is worth noting that the inflection point *I* occurs inside the chosen interval. Indeed, if *I* is not the sole stationary point in the system of differential equations (33), (34), then it is a saddle point. The farther *I* is from the origin, the broader interval $(\theta_{cr}, 0)$.

The problem is solvable at $\theta_\infty < \theta_{cr}$ or $\theta_\infty > 0$. Moreover, at any $\theta_\infty < \theta_{cr}$, for ω calculated from (39), there is a value of $\theta_1 > 0$ that defines another stable node, such that the second separatrix starting from the saddle singular point arrives there at $r \to +\infty$. Therefore, one more FHW propagates in the catalyst bed at the initial temperature θ_1 with the same velocity ω. At $\theta_\infty > 0$ and ω found from (39), the region of admissible θ values contains three stationary points of system (33), (34) if $f(-1/\beta) > 0$. Then, problem (33)–(36) is solvable at two values of the parameter θ_∞. Conversely, if $f(-1/\beta) < 0$, problem (33)–(36) is solvable at a single θ_∞ value.

A similar line of reasoning applies equally well to the values of the parameters of the model at which the inflection point lies to the right of $(0,0)$. There is an interval $(0, \theta_{cr})$ of θ_∞ values within which the problem has no solution. At $\theta_\infty < 0$, there are always three intersection points of null isoclines; at $\theta_\infty > \theta_{cr}$, there are three such points if $f(-1/\beta) > 0$ and two points if $f(-1/\beta) < 0$.

Figure 3 illustrates the FHW propagation velocity versus the initial temperature of the catalyst bed for two sets of

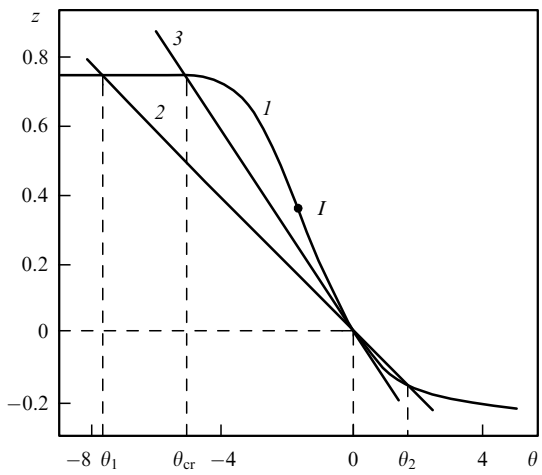

Figure 2. Null isoclines of system (33), (34): *1* — thermodynamic equilibrium curve, *2* — heat balance null isocline, *3* — tangent to curve *1* at the point $(0,0)$; *I* — inflection point of curve *1*.

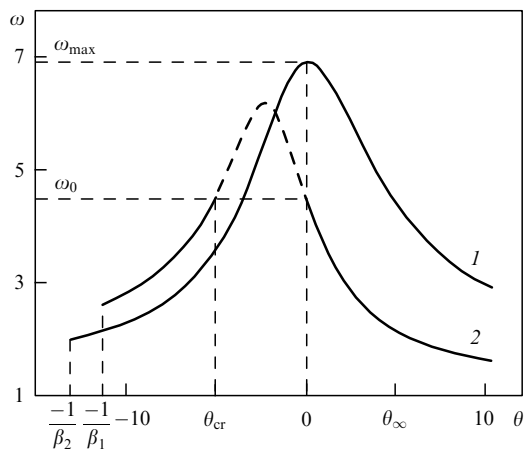

Figure 3. Dimensionless velocity of FHW propagation versus initial temperature: *1* — input conditions correspond to inflection point *I*, $T_0 = 469.7\,^\circ$C; *2* — input conditions correspond to $T_0 = 593.7\,^\circ$C.

parameters differing only in the input temperature T_0. The values $-1/\beta_1$ and $-1/\beta_2$ correspond to absolute zero temperature for curves *1* and *2*. At $\theta_\infty \to 0$ and $\theta_\infty \to \theta_{cr}$, the velocity ω tends to a maximum value ω_0. If the initial point $(0,0)$ is the inflection point I of the thermodynamic equilibrium curve, ω has the largest possible value ω_{max} provided all other parameters of the system (curve *1* in Fig. 3) are constant. Otherwise, there is a range of initial temperatures (213.1 – 593.7 °C for curve *2*) within which problem (33) – (36) is unsolvable even if ω can be computed. In this case, there are two more singular points, besides $(0,0)$. The one nearer to $(0,0)$ is a saddle and the velocity ω calculated from (39) corresponds to a FHW in which the transition occurs from this thermodynamic equilibrium point to zero conditions in the system under consideration. Invariance in the computation of ω arises from the invariance of the mass and energy conservation laws.

As the initial temperature of the catalyst bed grows indefinitely, $\omega \to 1$. When the initial temperature θ_∞ drops to $-1/\beta$, the velocity ω also decreases tending to a limit value ω_- that is larger than unity (see the Appendix). It is noteworthy that two FHWs may have the same velocity ω; in one of them, transition to the initial conditions with a higher temperature occurs, while in the other, the transition is to conditions with a lower temperature. Evidently, the character and the intensity of dissipative processes in these two waves are different. Hence, their structure must also be different.

Figure 4 shows the temperature and concentration profiles along a catalyst bed calculated from (33) – (36) for different initial and input temperatures. If $(0,0)$ is the inflection point I, the FHW propagation regime is realized at any temperature T_n (examples are given in Fig. 4). Conversely, if the input conditions correspond to a point lying to the right of point I on the thermodynamic equilibrium curve, as in Fig. 2, there is a range of initial temperatures at which no FHW is formed in the catalyst bed. In that case, there is a certain dynamic regime in the catalyst bed at $T_n = 213.1 - 593.7$ °C that does not lead to the formation of a heat wave structure with an asymptotic value of temperature T_n. In FHWs, the temperature monotonically varies along the catalyst bed from T_0 to T_n, as do the reactant concentrations from equilibrium values at the input to the equilibrium values corresponding to T_n, because the respective trajectories do not cross the null isoclines on the phase plane of system (33), (34).

At $T_n > T_0$, the level of substance B in the FHW front decreases and the heat is absorbed in the course of the reaction. At elevated temperatures, the high reaction rate constant determines the rate at which the concentration evolves towards equilibrium. Therefore, the value of z in each section along the catalyst bed is quasi-stationary and close to the equilibrium value $z_e(\theta)$. This is a fast variable in the system of equations. The phase trajectory in the high-temperature range runs close to the thermodynamic equilibrium curve. As T_n increases, the front width and propagation velocity along the bed decrease.

At $T_n < T_0$, reactant B is formed and the process proceeds with heat release. In the low-temperature range, where the reaction velocity constant is small, the solution is characterized by narrow temperature and concentration gradients along the catalyst bed. With decreasing T_n, this range broadens progressively and the part of it where the temperature and concentration profiles assume asymptotic values

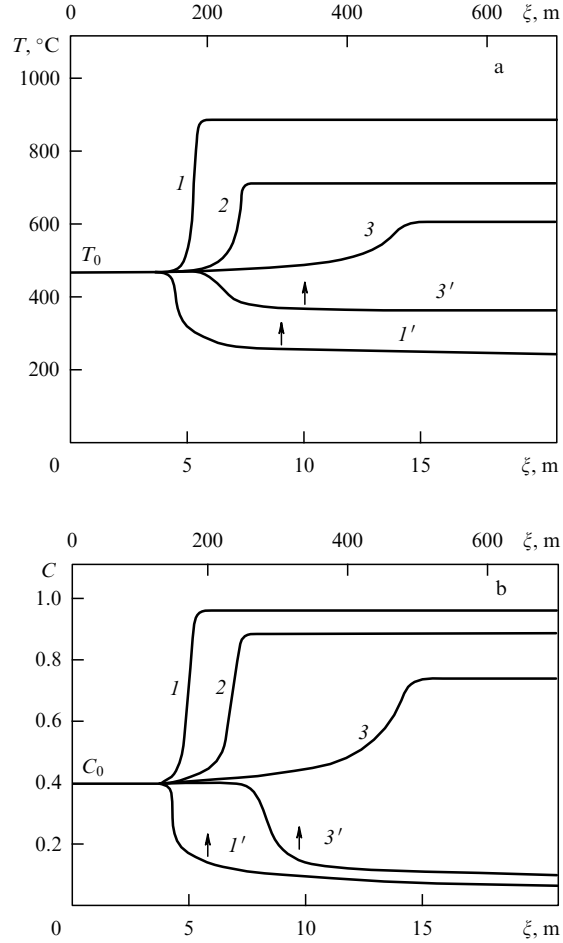

Figure 4. Profiles of the temperature (a) and reagent A dimensionless concentration (b) along the space – time coordinate at $T_0 = 469.7$ °C corresponding to the inflection point on the thermodynamic equilibrium curve at different time moments: curves *1*, *1′* — $\omega = 3.483$, $T_n = 870$ °C, $T_n' = 182.3$ °C; curves *2* — $\omega = 4.711$, $T_n = 700$ °C; curves *3*, *3′* — $\omega = 5.859$, $T_n = 595.7$ °C, $T_n' = 361.4$ °C.

becomes markedly extended. Here, the concentration is a slow and the temperature a fast variable in the system of equations (33), (34) because of the smallness of $K(\theta)$. This accounts for the trajectory in the phase plane running near the heat balance isocline. It is worth noting that the temperature and concentration gradients along the catalyst bed for two FHWs traveling with an equal velocity ω (curves *1*, *1′* and *3*, *3′* in Fig. 4) differ by several orders of magnitude.

As the initial temperature tends to zero ($\theta_\infty \to 0$), the temperature and concentration profiles in FHW increasingly gently slope and the front broadens due to the process proceeding in the immediate proximity to both the thermodynamic equilibrium curve and the heat balance null isocline.

Thus, the existence of FHWs directly follows from the analysis of the model in question and does not require any additional assumptions. For FHWs, the asymptotic value of the temperature θ_∞ at $r \to +\infty$ equals the initial temperature of the catalyst bed, ω is found from Eqn (39) based on the 'external' laws of mass and energy conservation alone, and the front shape 'adjusts itself' to these laws. Therefore, the FHW propagation velocity ω depends only on physicochemical properties of the reaction mixture and on the input and initial temperatures; at the same time, it is independent of the heat conduction of the catalyst bed and the kinetics of the

chemical reaction. An FHW may be an autowave resulting either from heating or cooling and able to propagate only in the direction of gas filtration ($\omega > 1$).

2.4 Necessary conditions for the existence of slow heat waves

Numerous experimental data suggest the possibility of SHW propagation during filtration of a cold reaction mixture through a preliminarily heated static catalyst bed [50–61, 66, 180]. Under real conditions, the starting reagent is chosen to be in a nonequilibrium state at low temperature, when no chemical reaction actually occurs. However, the chemical transformation rate at nonzero temperatures is higher than zero, $v(T, z) > 0$, in agreement with the Arrhenius law. This leads to the conclusion that neither the strictly stationary regime of SHW propagation in the catalyst bed nor the combustion front propagation in a homogeneous medium [42–45] is feasible. An approximate solution of the SHW steady propagation problem can be obtained by an artificial 'cut-off' (nullifying) of the reaction rate at low temperatures, universally accepted in the combustion theory. It consists of introducing a certain temperature below which the reaction rate may be regarded as identically vanishing. This method has been employed in Refs [62, 63, 65, 66, 68] to study SHWs. Because the phase portrait of a system (its singular points) is of special interest, it is appropriate, from the mathematical standpoint, to extend the temperature range as far as absolute zero [71]. Such idealization refers only to physical constraints on the possibility of reaching such low temperature and does not apply to mathematical simulation. Hence, the question of whether SHWs exist can be addressed without imposing additional restrictions on the function $v(T, z)$. If the input conditions are chosen as $T_0 = 0$ K, the integration constant in Eqn (22) vanishes ($N = 0$) and problem (23)–(26) acquires the form

$$\frac{\mathrm{d}T}{\mathrm{d}r} = (1-\omega)T - T_{\mathrm{ad}}(1-\alpha\omega)z\,, \tag{41}$$

$$\frac{\mathrm{d}z}{\mathrm{d}r} = K_2(T)\,\frac{z_{\mathrm{e}}(T) - z}{1-\alpha\omega}\,, \tag{42}$$

$$r \to -\infty: \qquad T \to 0\,, \qquad z \to 0\,, \tag{43}$$

$$r \to +\infty: \qquad T \to T_\infty\,, \qquad z \to z_{\mathrm{e}}(T_\infty)\,. \tag{44}$$

The problem of steady SHW propagation is reduced to solving (41)–(44). As pointed out above, the bounded solution of the problem, if it exists, converges at $r \to \pm\infty$ to the singular points of the system, i.e., the intersection points of null isoclines $z = z_{\mathrm{e}}(T)$ and the point

$$z = \frac{(1-\omega)T}{(1-\alpha\omega)T_{\mathrm{ad}}}\,. \tag{45}$$

The first singular point, defined by the input conditions at minus infinity, is a complex equilibrium state: the matrix of the system linearized in its vicinity has zero and positive eigenvalues. The second singular point, defined by the conditions at plus infinity, is a saddle at $\omega < 1$ (see the Appendix, Corollary 1.1). This implies that the reaction mixture is in the thermodynamic equilibrium behind the wave front at $r \to +\infty$, while ahead of the front at $r \to -\infty$, the temperature must tend to 0 K. Otherwise, the solution does not satisfy conditions (43), (44). Therefore, the only solution of the problem in the given case is a saddle separatrix. Integral energy balance (31) that relates the parameters ω and T_∞ can be written as

$$\omega = \frac{T_\infty - T_{\mathrm{ad}} z_{\mathrm{e}}(T_\infty)}{T_\infty - \alpha T_{\mathrm{ad}} z_{\mathrm{e}}(T_\infty)}\,. \tag{46}$$

For SHWs, the value of $\omega(T_\infty)$ is initially unknown and should be sought in the course of solving the problem. The parameter to be found, ω, must be such that the solution of the set of equations (41), (42) at any r remain in the physical volume of the phase space. At $\omega \to 1$, the degree of transformation $z \to 0$, and Eqn (46) implies the estimate

$$T_{\max} = \frac{q}{R \ln\left[(1 - z_{\mathrm{A},0})/(z_{\mathrm{A},0} k_{\mathrm{e}})\right]}\,.$$

Here, the maximum temperature is defined as a thermodynamically equilibrated temperature for the input reagent concentrations.

By choosing the temperature of the catalyst bed at plus infinity as T_∞, it is possible to calculate the equilibrium degree of transformation $z_{\mathrm{e}}(T_\infty)$ and ω from relation (46). This, in turn, makes it possible to numerically construct a separatrix entering the equilibrium point $(T_\infty, z_{\mathrm{e}}(T_\infty))$ by integrating system of equations (41), (42) in the direction opposite to that of the vector field (in 'inverse' time). Our calculations were made at the aforementioned parameters of the model.

A numerical experiment has demonstrated that separatrixes of system (41), (42) that arise at sufficiently high temperatures T_∞ at plus infinity intersect the axis of temperatures $z = 0$ at $T > 0$ K (Fig. 5, curves *4*, *5*). That is, they leave the physical domain of the phase space and fail to satisfy boundary conditions (43). (Examples of the results of computations of the respective temperature profiles in the space–time variable are given in Fig. 6.) At sufficiently low values of the temperature T_∞, the trajectories reach the heat balance null isocline (45) at nonzero temperatures and degrees of reagent transformation; they further move in the vicinity of (45) and reach input values for a finite (albeit rather large) 'time' r_0 (curves *1* and *2* in Fig. 5). All these trajectories

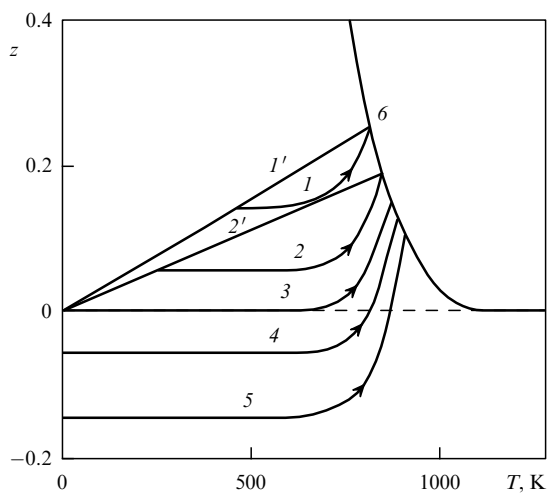

Figure 5. Trajectories of system of equations (41), (42) on the phase plane at temperatures on plus infinity: curve *1* — 850 K, *2* — 880 K, *3* — 900 K, *4* — 915 K, *5* — 940 K, *6* — thermodynamic equilibrium curve, *1′*, *2′* — heat balance null isoclines.

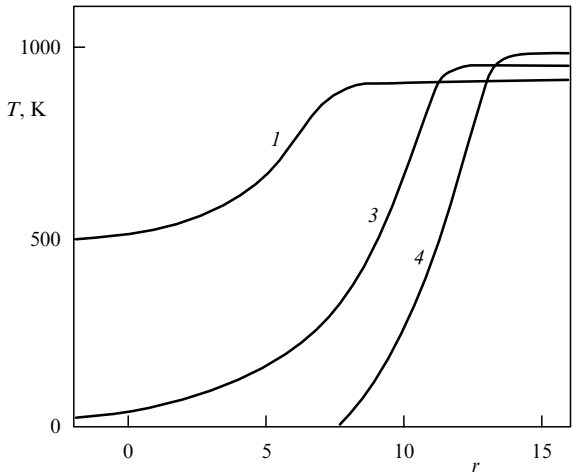

Figure 6. Temperature profiles along the catalyst bed (curve numbers correspond to the numbers of trajectories shown in Fig. 5).

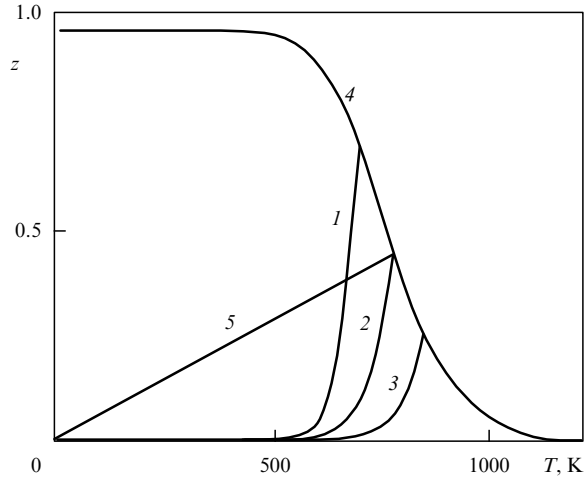

Figure 7. SHW trajectories on the phase plane for different values of the reaction rate constant k_0: 0.5862×10^{11} s^{-1} (curve *1*), 0.42645×10^{10} s^{-1} (curve *2*), 0.369×10^{9} s^{-1} (curve *3*), *4* — thermodynamic equilibrium curve, *5* — heat balance null isocline for trajectory (2).

are characterized by a short 'time' needed to reach the heat balance null isocline and a 'slow' motion in its neighborhood towards the point $(0, 0)$. Hence, there is no heating zone for the cold front segment in which only the reaction mixture temperature increases and the degree of reagent transformation is zero.

We emphasize that at low temperatures, the separatrix goes very closely together with the heat balance null isocline but cannot cross it; this inference follows from the analysis of the vector field of system (41), (42). If a desired degree of transformation at low temperatures is to be reached, the contact time must be sufficiently large, the reaction zone being markedly extended. It may be stated that the part of the trajectory on which 'fast' movement of the image points occurs should be regarded as an intermediate asymptotic regime of the solutions [188]. All these trajectories are mathematically equivalent solutions of the problem but not all of them are consistent with the physical notion of heat waves. The one-parameter family of mathematically equivalent solutions of the problem includes a single trajectory at which the reactant concentrations assume input values at nonzero temperatures. This trajectory approaches the point $(0, 0)$ horizontally, along the axis of temperatures (curve *3* in Fig. 5). As the degree of transformation has attained its input value, it becomes 'frozen' and no longer changes with decreasing the temperature, which varies in accordance with the equation $\mathrm{d}T/\mathrm{d}r = (1 - \omega)T$ (curve *3* in Fig. 6). Characteristic of this trajectory is the fact that the reaction rate can be nullified at higher temperatures than the input temperature, with the solution being independent of the so-called temperature 'cut-off' [62, 63, 65, 66, 68]. This trajectory is an FHW image. We note that this is possible when $\omega < 1$, the value of ω being the maximum one among all mathematically equivalent solutions.

Interestingly, relation (46), which expresses energy balance in SHWs, does not contain the rate constant of the chemical reaction. It proves possible to change the system's phase trajectory by varying k_0 such that it corresponds to the physically meaningful solution with a temperature $T_\infty < T_{\max}$ chosen in advance and, moreover, such that it propagates with a predetermined velocity. Hence, for a simple kinetic model, k_0 can be deduced from the experimentally found values of T_∞ and ω. When T_∞ equals the temperature of the adiabatic heating of the reaction mixture T_{ad}, it is natural to expect that $\omega = 0$. Indeed, it follows from (46) that the solution of problem (41)–(44) has the form of a standing heat wave. Furthermore, Eqn (46) gives $\omega < 0$ for $T_\infty < T_{\mathrm{ad}}$, and the solution of the problem is an SHW propagating counter to the filtered gas flow. For $T_\infty > T_{\mathrm{ad}}$, Eqn (46) yields $0 < \omega < 1$ and the SHW has the same direction as gas filtration.

Examples of the corresponding phase trajectories and temperature profiles along a catalyst bed are presented in Figs 7 and 8. As is clear from Fig. 8, SHWs running against the gas flow have larger temperature gradients over the front than those traveling in the direction of gas filtration.

If the temperature of the reaction mixture at the entry to a catalyst bed is $T_0 > 0$, the rate of the chemical reaction $v(T_0, z) > 0$. Then, if the reaction rate under the input conditions remains nonzero, the point at $r \to -\infty$ is not stationary and, strictly speaking, the problem is ill-posed. However, it would be wrong to conclude that SHW propagation at a low (but nonzero) input temperature is physically impossible. At $T_0 > 0$ K, it is worth passing to the dimensionless temperature θ, i.e., to problem (33)–(36), in order to numerically investigate phase trajectories of system (33), (34) by 'inverse time' integration, without resorting to the artificial 'cut-off' of the reaction rate at low temperatures. Our calculations were made at the parameters of the model described above for a sufficiently broad range of catalyst bed temperatures at $r \to \pm\infty$. It should be recalled that the SHW propagation velocity $\omega < 1$ is related to the maximum temperature θ_∞ by energy balance equation (39).

In the theory of dynamic systems [116, 117], part of a complete trajectory containing one of the singular points is referred to as a semitrajectory. Figure 9 gives examples of semitrajectories of system (33), (34) on the phase plane (θ, z). The phase portrait of the system is similar to that at $T_0 = 0$ K. Some of the semitrajectories leave the physical domain of the phase space, crossing the axis of temperatures at $\theta > 0$ ($T_0 = 300$ K). Others approach the heat balance null isocline (37) as r decreases, then pass close to it and enter the region with $z < 0$ near the point $(0, 0)$. These semitrajectories have long segments with small temperature and concentration

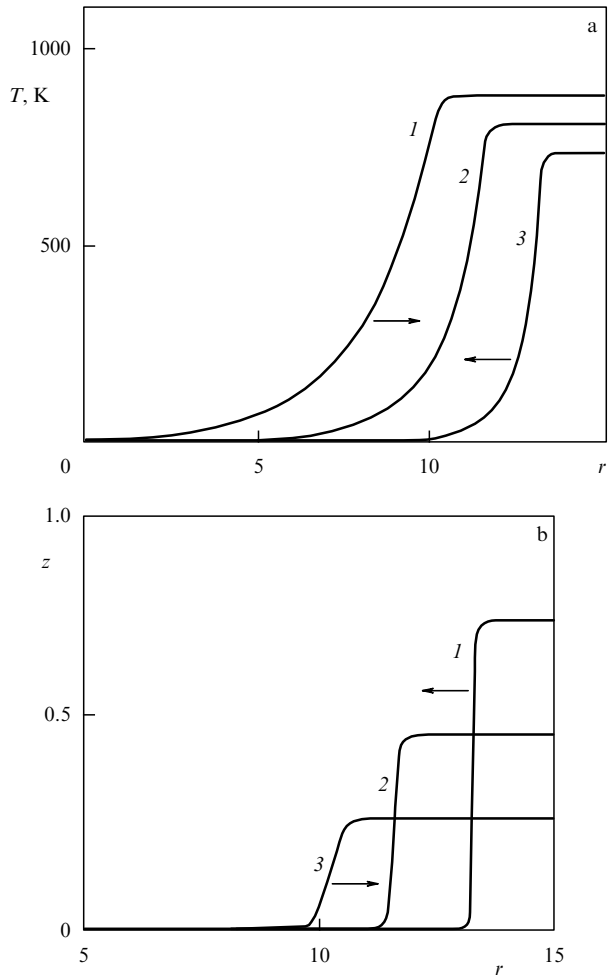

Figure 8. Profiles of the temperature (a) and degree of reagent A transformation (b) in the space–time variable for different SHWs (numbers of the curves correspond to those in Fig. 7; arrows show the direction of SHW motion).

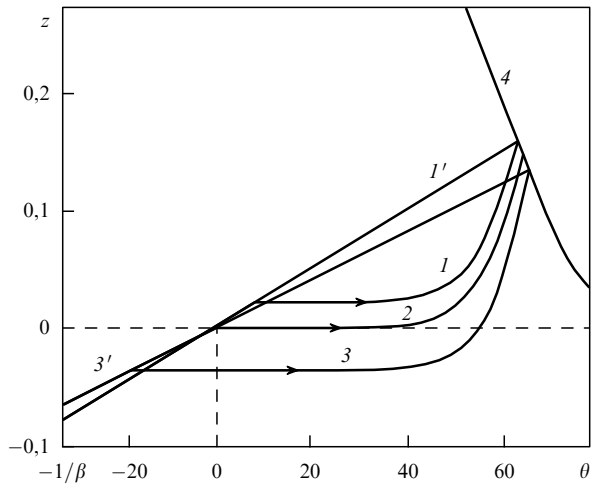

Figure 9. Trajectories of system of equations (33), (34) on the phase plane at $T_0 = 0$ K: curve *1* — $\theta_\infty = 65.98$, curve *2* — $\theta_\infty = 66.84$, curve *3* — $\theta_\infty = 68.22$ (*1′* and *3′* — heat balance null isoclines, *4* — thermodynamic equilibrium curve).

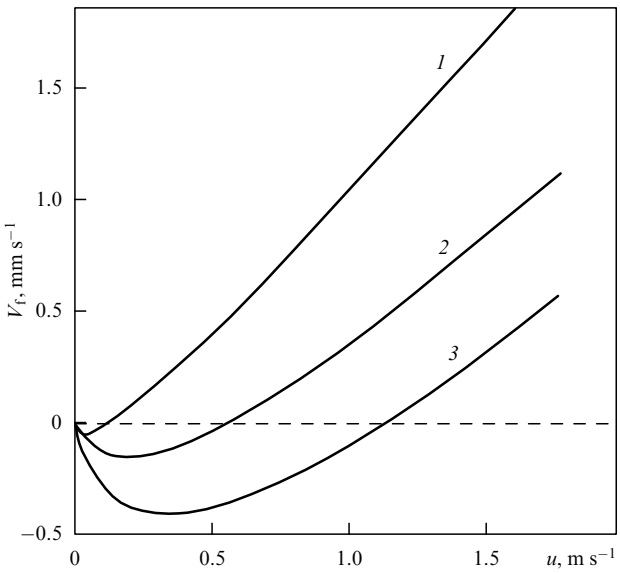

Figure 10. Plots of the SHW propagation velocity vs the gas filtration rate at different parameters of the model: curve *1* — $k_e = 5.737 \times 10^{-5}$, $T_0 \to 0$ K; curve *2* — $k_e = 10^{-3}$, $T_0 \to 0$ K; curve *3* — $k_e = 10^{-3}$, $T_0 \to 300$ K.

gradients over r, which are not observed in experiment. From the continuum of semitrajectories, we can choose a single one passing near the origin such that the corresponding reactant concentrations reach the input values at higher temperatures than at the entry to the catalyst bed (curve *2* in Fig. 9). This semitrajectory is consistent with the artificial 'cut-off' of the reaction rate at low temperatures and is an image of SHWs.

We emphasize that motions of the image point along the heat balance isocline are impossible at zero reaction rate; it can move only parallel to the axis of temperatures, concentrations of the reactants remaining unaltered. The dimensionless SHW rate $\omega = 0.538$ shown by curve *2* in Fig. 9 corresponds to $V_f = 0.768 \times 10^{-3}$ m s^{-1}. The rate of gas filtration $u = 1$ m s^{-1} is approximately three orders of magnitude greater than that of SHW propagation. Such a large difference between the rates is attributable to the difference between volume heat capacities of the solid and gaseous phases. The flow of gas being filtered brings fresh material into the reaction zone, and the temperature behind the wave front is much higher than that of the adiabatic heating of the reaction mixture. The fresh gas flow 'washes out' possible changes in the reactant concentrations due to chemical reactions proceeding at low temperatures ahead of the wave front.

The SHW propagation velocity is one of the principal parameters of technological interest. It is worth noting that analytical estimation of the SHW propagation velocity for reversible reactions poses some difficulty because the reactant concentrations depend on the maximum temperature. We therefore undertook a numerical study on the effect of model parameters on the SHW propagation velocity. Figure 10 shows extremal $V_f(u)$ dependences for different input temperatures and equilibrium constants of the reaction. It can be seen that low gas filtration rates are associated with the on-coming motion of heat waves. There is only one value of the gas filtration rate at which the standing SHW regime is realized. Further increase in the gas filtration rate is accompanied by a roughly proportional rise in the SHW propagation velocity. Taken together, the elevation of

temperature at the entry to the catalyst bed and the enhancement of the reaction equilibrium constant lead to the broadening of the range of the gas filtration rates at which the regime of on-coming heat wave motion is realized. Generally speaking, the velocity V_f falls with a rise in the above parameters.

We now turn to qualitative differences between FHWs and SHWs. The existence of FHWs is immediately apparent from the analysis of the model under consideration and requires no additional assumptions. In contrast, the existence of SHWs is proved only if the reaction rate cut-off at low temperatures is introduced. For FHWs (unlike SHWs), the asymptotic temperature value at $r \to +\infty$ is equal to the initial one in the catalyst bed, the value of ω is found from the 'external' laws of mass and energy conservation using Eqn (39), and the front shape 'adapts itself' to these laws. An FHW is a wave of either heating or cooling. In SHWs, the catalyst bed is always cooled by the convective gas flow, and the heat released during the exothermal reaction interferes with cooling. When the front temperature in an FHW increases, cooling of the catalyst bed by the convective gas flow is always accompanied by heat absorption necessary to maintain the endothermal reaction. This characteristic difference accounts for the existence of a barrier that separates the FHW and SHW propagation velocities, $\omega > 1$ for FHWs and $\omega < 1$ for SHWs.

We conclude this section with the following summary.

We have investigated the behavior of phase trajectories of a quasi-homogeneous AWP model in a static catalyst bed without introducing any additional assumptions. The existence of space – time structures (traveling waves) is mathematically substantiated by the presence of special trajectories in the automodel system that connect stationary (singular) points. It has been shown that a reversible reaction in the catalyst bed gives rise to an FHW, besides an SHW, that has the same direction as the gas flow. Categorization of autowaves into FHWs and SHWs is needed because their characteristics are qualitatively different. In the first place, this is true of the autowave propagation velocity. The role of the separating 'barrier' is played by the velocity of a heat label in the catalyst bed in the absence of chemical transformation. This velocity is given by the gas filtration rate times the ratio of gas to catalyst specific heat capacities. The phenomenon of FHW propagation affords an example of the appearance of a space – time dissipative structure not only far from the system's thermodynamic equilibrium but also close to it.

The SHW propagation problem is proved to have a one-parameter family of separatrix trajectories from which the sole physically meaningful solution must be chosen. Major principles of SHW propagation have been analyzed.

It should be noted that the quasi-homogeneous model of a static catalyst bed is identical to the mathematical description of processes of homogeneous filtering combustion in which the heat exchange between phases is sufficiently intense and differences between gaseous and solid phase temperatures can be a priori neglected. In this case, all the above results remain valid for a reversible homogeneous reaction proceeding in an inert granular layer.

In technological processes involving periodically reversed gas flows, the high-temperature reaction zone moves with the flow towards the cooled portion of the catalyst bed. In the case of reversible reactions, a transition occurs from high equilibrium temperatures in the central part of the catalyst bed to lower temperatures at the outlet [66, 180]. This part of the catalyst bed is the site of FHW formation that may be incomplete for the time spent between switching from one regime to the other and back. The process repeats after each change in the gas flow direction. Concentration of the reaction product increases along the length of the catalyst bed with the downward temperature profile. An additional amount of the product thus formed depends on both the temperature profile and the front propagation velocity. This implies that the knowledge of major FHW characteristics may be of great help in the search for optimal technological conditions of reversible reactions involving the reverse gas flow regime (flow rate, input temperature, concentration of the reagents, thermophysical properties of the catalyst bed, etc.).

3. Nonequilibrium thermodynamics of autowave processes

3.1 Basic equations

Current developments in nonequilibrium thermodynamics are inseparable from the construction of the theory of nonlinear processes in strongly nonequilibrium systems. Nonequilibrium thermodynamics arose as a result of the extension of classical thermodynamics to embrace minor deviations of a system from equilibrium. Linear thermodynamics of irreversible processes was pioneered by L Onsager [133].

We briefly recall several postulates of nonequilibrium thermodynamics. In equilibrium systems, thermodynamic forces X_i and flows J_i vanish. In the linear regime, the system's behavior in time is described in the most general case by linear phenomenological equations [113, 134, 138, 140, 189, 190]

$$J_i = \frac{\mathrm{d}a_i}{\mathrm{d}t} = \sum_k L_{ik} X_k \,, \tag{47}$$

where L_{ik} denotes phenomenological, or kinetic, coefficients and a_i are the internal parameters (state variables) that for open systems depend not only on internal microscopic quantities but also on external influences.

State variables may be either even or odd functions of particle velocities. We are interested only in the case where state variables are even functions of particle velocities; therefore, we do not need the general form of the Onsager – Casimir relations [189, 191] that includes both cases.

The matrix $\boldsymbol{L}$ is positive definite; its diagonal elements L_{ii} determine 'direct' transfer phenomena and nondiagonal ones, L_{ik}, satisfying Onsager's reciprocal relations ($L_{ik} = L_{ki}$), define 'reciprocal' (or 'conjugate') processes. In isotropic systems, only the relations between fluxes and forces of the same tensor dimension are retained in agreement with the Curie principle of conservation of symmetry between action and reaction.

In the first approximation, the expressions for the entropy deviation ΔS from equilibrium is written as a quadratic form in state variables [134, 138, 189],

$$\Delta S = -\frac{1}{2} \sum_i \sum_k g_{ik} a_i a_k \,, \tag{48}$$

where g_{ik} are the second derivatives of ΔS in the variables a_i (this is a positive definite matrix).

We note that Onsager's reciprocal relations hold if thermodynamic forces are defined by the expression

$$X_i = \frac{\partial \Delta S}{\partial a_i} = -\sum_k g_{ik} a_k \,. \tag{49}$$

The entropy increase ΔS can be used as the Lyapunov function having properties of a potential [113, 114, 119–121, 130]. Its total time derivative can be written as

$$\frac{\mathrm{d}\Delta S}{\mathrm{d}t} = -\sum_i \sum_k g_{ik} a_k \frac{\mathrm{d}a_i}{\mathrm{d}t} = \sum_i J_i X_i \,. \tag{50}$$

Elementary changes in entropy in the general form are described by the equation

$$\mathrm{d}S = \mathrm{d_r}S + \mathrm{d_i}S \,, \tag{51}$$

formulated by Clausius. The total change of entropy in the system $\mathrm{d}S$ is the sum of the external (or reversible) change $\mathrm{d_r}S = \delta_\mathrm{r}Q/T$ associated with the reversible heat exchange $\delta_\mathrm{r}Q$ between the system and the environment at the absolute temperature T and of a positive change in entropy $\mathrm{d_i}S \geqslant 0$ due to irreversible processes inside the system. These relations reflect the Carnot–Clausius theorem, i.e., the second law of thermodynamics, in the general form.

In the thermodynamics of continuum, general relation (51) must be formulated in a local form. This requires assuming the hypothesis of local equilibrium in continuum systems [113, 134, 138, 140, 189]. This hypothesis allows us to apply parameters of thermostatic equilibrium and their interrelations to nonequilibrium systems. It is supposed that the Gibbs relation is applicable to the unit mass of any elementary region of the continuum [113, 134, 138, 140, 189],

$$T\,\mathrm{d}s = \mathrm{d}h - \frac{1}{\rho}\,\mathrm{d}p - \sum_{k=1}^{n} \mu_k M_k \,\mathrm{d}y_k \,, \tag{52}$$

which unifies the first and the second principles of thermodynamics for equilibrium systems in their standard form. Here, s is the unit mass entropy, ρ is the total density, p is the pressure, h is the unit mass enthalpy, μ_k is the chemical potential of the kth component per mole, and y_k is the mass concentration of the kth component. Then, the total entropy of the system is described by the expression

$$S = \int_V \rho s \,\mathrm{d}V \,. \tag{53}$$

Under conditions of local equilibrium at an arbitrary internal point of the continuum, the second law of thermodynamics is described by the local balance equation [113, 134, 138, 140, 189)

$$\frac{\partial \rho s}{\partial t} = -\mathrm{div}\, J_{S,\Sigma} + \sigma \tag{54}$$

or the substantial balance equation

$$\rho\,\frac{\mathrm{d}s}{\mathrm{d}t} = -\mathrm{div}\, J_S + \sigma \,. \tag{55}$$

Here, $J_{S,\Sigma}$ is the local density of the entropy flow, J_S is the substantial density of the entropy flow, and

$$\sigma = \sum_i J_i X_i$$

is the entropy source intensity, or local entropy production.

The total entropy production in the system, P, is

$$P = \frac{\mathrm{d_i}S}{\mathrm{d}t} = \int_V \sigma\,\mathrm{d}V \geqslant 0 \,. \tag{56}$$

3.2 Entropy balance equation and entropy production in a catalyst bed

The entropy balance equation plays the central role in nonequilibrium thermodynamics. The concrete form of this equation is found by substituting the enthalpy (internal energy) balance equation into the Gibbs equation and simultaneously eliminating the derivatives of component concentrations with the help of the component balance equation [113, 134, 138, 140, 189].

In the system of coordinates associated with a traveling front, enthalpy balance (4) for steady-state solutions acquires the form

$$\frac{\mathrm{d}}{\mathrm{d}\xi}\left(\rho_\mathrm{g} u h_\mathrm{g} - \varepsilon_\mathrm{g} V_\mathrm{f}\,\rho_\mathrm{g} h_\mathrm{g} - \varepsilon_\mathrm{c} V_\mathrm{f}\,\rho_\mathrm{c} h_\mathrm{c}\right) = -\frac{\mathrm{d}J_q}{\mathrm{d}\xi} \,. \tag{57}$$

Substituting (57) in Gibbs equation (52) and eliminating the derivatives of component concentrations with the help of Eqn (14), we obtain the entropy balance equation

$$\frac{\rho_\mathrm{g} u c_p}{\lambda}\,\frac{\mathrm{d}}{\mathrm{d}r}\left((1-\alpha\omega)\,\rho_\mathrm{g} u s_\mathrm{g} - \frac{\omega}{\gamma}\,u\varepsilon_\mathrm{c}\rho_\mathrm{c} s_\mathrm{c}\right) = \frac{Av}{T} - \frac{\rho_\mathrm{g} u c_p}{\lambda}\,\frac{1}{T}\,\frac{\mathrm{d}J_q}{\mathrm{d}r} \,, \tag{58}$$

where $s_\mathrm{g} = (\rho_\mathrm{A} s_\mathrm{A} + \rho_\mathrm{B} s_\mathrm{B})/\rho_\mathrm{g}$ and s_c are the gas and catalyst entropies per unit mass, respectively, and

$$A = -\sum_k \chi_k \mu_k = RT \ln \frac{K_p(T)C}{1-C}$$

is the chemical affinity of the reaction. (The affinity A is always constant for a given state regardless of the nature of the transformation that takes place in the system.)

Equation (58) is at variance with the equation for substantial balance of entropy of type (55). But if the known relation [113, 134, 138, 140, 189]

$$\frac{1}{T}\,\nabla\cdot J_q = \nabla\cdot\frac{J_q}{T} - J_q\cdot\nabla\frac{1}{T}$$

is used, Eqn (58) can be written as

$$\frac{\rho_\mathrm{g} u c_p}{\lambda}\,\frac{\mathrm{d}}{\mathrm{d}r}\left((1-\alpha\omega)\,\rho_\mathrm{g} u s_\mathrm{g} - \frac{\omega}{\gamma}\,u\varepsilon_\mathrm{c}\rho_\mathrm{c} s_\mathrm{c} - \frac{\rho_\mathrm{g} u c_p}{T}\,\frac{\mathrm{d}T}{\mathrm{d}r}\right) = \frac{Av}{T} + \frac{(\rho_\mathrm{g} u c_p)^2}{\lambda T^2}\left(\frac{\mathrm{d}T}{\mathrm{d}r}\right)^2 \,. \tag{59}$$

The right-hand side of Eqn (59) describes local entropy production in the system,

$$\sigma = \sigma_\mathrm{ch} + \sigma_q = \frac{Av}{T} + \frac{(\rho_\mathrm{g} u c_p)^2}{\lambda T^2}\left(\frac{\mathrm{d}T}{\mathrm{d}r}\right)^2 \geqslant 0 \,, \tag{60}$$

which consists of two components: σ_ch is the local entropy production resulting from chemical reaction and σ_q is the local entropy production due to heat transfer.

For chemical reactions, linear relations of nonequilibrium thermodynamics hold near equilibrium when the condition $A \ll RT$ is satisfied. This does not mean, however, that

nonequilibrium thermodynamics is unfit for describing chemical reactions [114]. Analysis based on the kinetic theory of gases indicates that the expression $\sigma_{\rm ch} = Av/T$ is valid for those reactions for which the law of mass action is fulfilled even if condition $A \ll RT$ is not satisfied [189, 192]. In this case, $\sigma_{\rm ch}$ is also a positive definite function. This follows from the definition of the chemical affinity of a reaction in which $Av > 0$ when the system evolves towards the global minimum (equilibrium).

For heat conduction described by the linear Fourier law, things are quite clear over the entire range of temperature variations. As is known, σ_q is a positive definite quadratic form in thermodynamic forces [113, 134, 138, 140, 189],

$$\sigma_q = J_q X_q = L_{qq} X_q^2 = \frac{(\rho_{\rm g} u c_p)^2}{\lambda T^2} \left(\frac{{\rm d}T}{{\rm d}r}\right)^2 = \frac{(\rho_{\rm g} u c_p)^2}{\lambda} T^2 \left(\frac{{\rm d}(1/T)}{{\rm d}r}\right)^2 \geqslant 0\,,$$

where

$$J_q = -\rho_{\rm g} u c_p \frac{{\rm d}T}{{\rm d}r} = \rho_{\rm g} u c_p T^2 \frac{{\rm d}(1/T)}{{\rm d}r}$$

is the heat flow,

$$X_q = -\frac{\rho_{\rm g} u c_p}{\lambda T^2} \frac{{\rm d}T}{{\rm d}r} = \frac{\rho_{\rm g} u c_p}{\lambda} \frac{{\rm d}(1/T)}{{\rm d}r}$$

is the thermodynamic force, and L_{qq} is a phenomenological coefficient.

It is also known that thermodynamic flows and forces of various tensor ranks cannot be interrelated, in agreement with Curie's principle of symmetry [113, 134, 138, 140, 189]. Therefore, Onsager's reciprocal relations play no important role in the case under consideration. It should be noted that Eqns (18), (57), and (59) are essentially equivalent, but the local entropy production (60) entering Eqn (59) contains qualitatively new information ($\sigma \geqslant 0$).

For a one-dimensional problem, the total entropy production in the system described by expression (56) is the integral over the space–time variable,

$$P = \int_{-\infty}^{+\infty} \sigma\, {\rm d}\ell = \frac{\lambda}{\rho_{\rm g} u c_p} \int_{-\infty}^{+\infty} \sigma\, {\rm d}r\,. \tag{61}$$

We now show that the total entropy production for all autowave solutions is a positive definite bounded function.

As shown above, autowave solutions in the case of FHW propagation correspond to a separatrix on the phase plane, connecting a saddle point with a stable node. All singular points (intersection points of null isoclines) are equilibrium points of the system. We note that null isocline (46) satisfies thermal equilibrium conditions of the system when there is no temperature gradient, i.e., $J_q = 0$ and $X_q = 0$ at the points of the null isocline. In other words, thermodynamic flows and forces vanish at the singular points ($v = 0$, $A = 0$, $J_q = 0$, $X_q = 0$). Then, it follows from Eqn (60) that in FHWs, $\sigma \to 0$ as $r \to \pm\infty$.

In the case of SHW propagation, the separatrix enters a saddle singular point determined by the conditions at $r \to +\infty$. In this case, thermodynamic flows and forces also vanish and $\sigma \to 0$. The second singular point determined by the conditions at $r \to -\infty$ is a point of a complex equilibrium state (intersection point of null isocline (46) and null isocline $T = 0$ K). But the boundary condition $T \to 0$ K, Eqn (43), does not mean that the separatrix is connected with a singular point inside the physical domain of the phase space. We recall that condition (43) has been obtained from condition (20) that split into two: $T \to 0$ K and the conductive heat flow tending to zero ($J_q \to 0$). Hence, in accordance with (20), the separatrix at $r \to -\infty$ must be connected with a singular point at which $J_q = 0$ and $X_q = 0$. The local entropy production due to chemical reaction also tends to zero ($\sigma_{\rm ch} \to 0$) at $T \to 0$ K as is easy to show by substituting (3) in (60) and finding the corresponding limit:

$$\lim_{T\to 0} \frac{Av}{T} = \lim_{T\to 0} R \ln\left(k_{\rm e} \exp\left(\frac{q}{RT}\right) \frac{C}{1-C}\right) \times k_0 C_0 \exp\left(-\frac{E}{RT}\right) C \left[1 - \frac{1-C}{C k_{\rm e} \exp\left(q/(RT)\right)}\right] = 0\,.$$

Thus, the local entropy production for autowave solutions of the problem is a positive definite bounded function of T and z that tends to zero as $r \to \pm\infty$. Because the autowave solutions for the problem are smooth bounded functions, the total entropy production in the system P is also a positive definite bounded function.

Equation (59) in dimensionless variables (17) and (32) takes the form

$$\frac{\rho_{\rm g} u c_p}{\lambda} \frac{\rm d}{{\rm d}r} \left((1-\alpha\omega)\, \rho_{\rm g} u s_{\rm g} - \frac{\omega}{\gamma}\, u \varepsilon_{\rm c}\, \rho_{\rm c} s_{\rm c} - \frac{\rho_{\rm g} u c_p \beta}{1+\beta\theta} \frac{{\rm d}\theta}{{\rm d}r}\right) = \sigma\,. \tag{62}$$

With (33), the expression for the local entropy production (60) can be represented as

$$\sigma = \frac{(\rho_{\rm g} u c_p)^2}{\lambda} \left[K(\theta)\left(z_{\rm e}(\theta) - z\right) \frac{RC_0}{\rho_{\rm g} c_p} \ln \frac{K_p(\theta)(z_{\rm A,0} - z)}{1 - z_{\rm A,0} + z} + \left(\beta\, \frac{(1-\omega)\theta - (1-\alpha\omega) Q z}{1+\beta\theta}\right)^2\right]. \tag{63}$$

Substitution of (63) in Eqn (61) yields

$$P = \rho_{\rm g} u c_p \int_{-\infty}^{+\infty} \left[K(\theta)\left(z_{\rm e}(\theta) - z\right) \frac{RC_0}{\rho_{\rm g} c_p} \ln \frac{K_p(\theta)(z_{\rm A,0} - z)}{1 - z_{\rm A,0} + z} + \left(\beta\, \frac{(1-\omega)\theta - (1-\alpha\omega) Q z}{1+\beta\theta}\right)^2\right] {\rm d}r\,. \tag{64}$$

Substituting (62) in (61), we obtain

$$P = \int_{-\infty}^{+\infty} \sigma\, \frac{\lambda}{\rho_{\rm g} u c_p}\, {\rm d}r = (1-\alpha\omega)\, \rho_{\rm g} u s_{\rm g} \Big|_{-\infty}^{+\infty} - \frac{\omega}{\gamma}\, u \varepsilon_{\rm c}\, \rho_{\rm c} s_{\rm c} \Big|_{-\infty}^{+\infty} - \frac{\rho_{\rm g} u c_p \beta}{1+\beta\theta} \frac{{\rm d}\theta}{{\rm d}r} \Big|_{-\infty}^{+\infty}. \tag{65}$$

It follows from the boundary conditions at $r \to \pm\infty$ that the flow of entropy due to heat conduction [the last term on the right-hand side of Eqn (65)] vanishes. Because the specific entropy s is a function of the parameters of state T, p, $z_{\rm A,0}$, and z alone, it follows from (65) that

$$P = (1-\alpha\omega)\, \rho_{\rm g} u\, \Delta s_{\rm g} - \frac{\omega}{\gamma}\, u \varepsilon_{\rm c}\, \rho_{\rm c}\, \Delta s_{\rm c}\,, \tag{66}$$

where $\Delta s_c = c_c \ln(1 + \beta\theta_\infty)$ is the increase in specific entropy of the catalyst,

$$\Delta s_g = \frac{\Delta S_T^0 \Delta z C_0}{\rho_g} - \frac{RC_0}{\rho_g}\big[(1 - z_{A,0})\ln(1 - z_{A,0}) + z_{A,0}\ln z_{A,0} - z_\infty \ln z_\infty - (1 - z_\infty)\ln(1 - z_\infty)\big] + c_p \ln(1 + \beta\theta_\infty)$$

is the increase in specific entropy of the reaction mixture, $z_\infty = z_e(\theta_\infty)$, and $\Delta z = z_\infty - z_{A,0}$.

Hence, the important conclusion is that the total entropy production P can be calculated using analytical formula (66) or integrating along the numerically computed separatrix trajectory according to Eqn (64).

3.3 Total entropy production in fast heat waves

The phenomenon of FHW propagation in a static catalyst bed is described by system of equations (33), (34) with boundary conditions (35), (36). Examples of computation of FHW characteristics are given in Figs 3 and 4. The temperature dependence of the total entropy production in FHW on plus infinity $P(\theta_\infty)$ for two values of the input temperature T_0 shown in Fig. 3 was calculated using Eqn (66) with (39) taken into account (Fig. 11).

If the point $(0, 0)$ is the inflection point I, the autowave solution of problem (33)–(36) exists at any θ_∞, with ω having the highest possible value ω_{max}.

Conversely, if the point $(0, 0)$ is not the inflection point I, there is a range of 'forbidden' temperatures $0 \leqslant \theta_\infty \leqslant \theta_{cr}$ ($213.1 \leqslant \theta_\infty \leqslant 593.7°$ for curve *2* in Fig. 11) in which problem (33)–(36) has no solution but $\omega(\theta_\infty)$ can still be found from (39) and $P(\theta_\infty)$ from (66). In this case, two other particular points besides point $(0, 0)$ exist. The point closest to $(0, 0)$ is then a saddle and ω calculated from (39) then corresponds to FHWs in which the transition might be possible from this point of thermodynamic equilibrium to the conditions corresponding to the origin of coordinates. Invariance in the computation of ω follows from the invariance of the mass and energy conservation laws. Computation of $P(\theta_\infty)$ using Eqn (66) for the 'forbidden' temperature range θ_∞ yields negative entropy production [which has no physical meaning and cannot be found from (64)]. It thus substantiates the existence of this interval by the methods of nonequilibrium thermodynamics. As θ_∞ approaches 0 or θ_{cr}, the total entropy production in the system decreases due to physico-chemical processes in the immediate proximity to both the thermodynamic equilibrium curve and the heat balance null isocline.

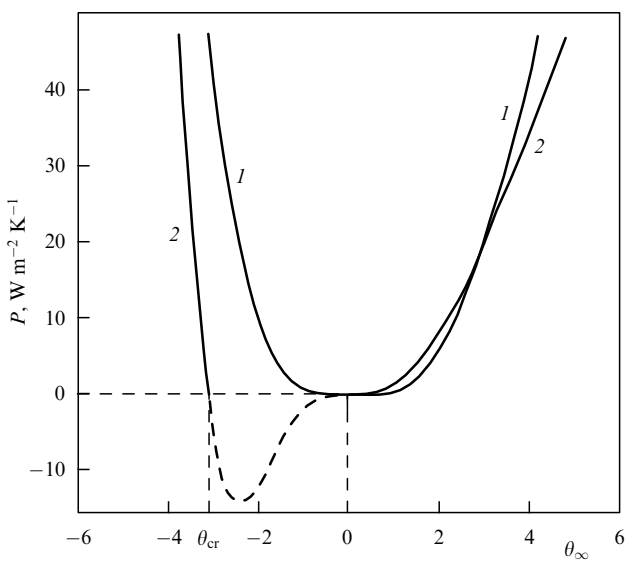

Figure 11. The total entropy production in FHW versus the dimensionless temperature at plus infinity (curves *1* and *2* correspond to the conditions in Fig. 3).

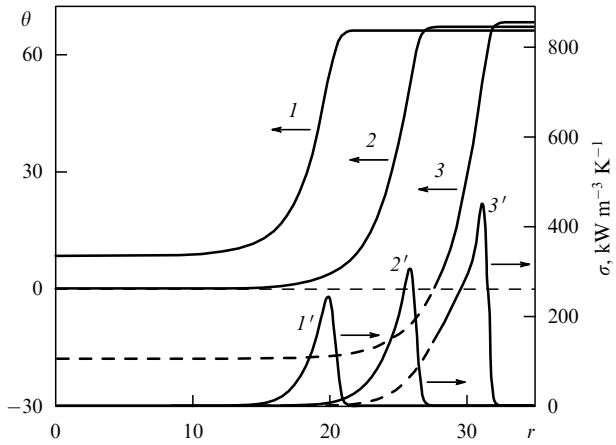

Figure 12. Profiles of the dimensionless temperature and distribution functions of local entropy production in a space–time variable for different trajectories of system (33), (34) (numbers of curves correspond to the numbers of trajectories shown in Fig. 9).

3.4 The principle of minimum total entropy production in SHWs. Variational formulation of the problem

In the propagation of SHWs, in contrast to FHWs, the temperature θ_∞ is unknown a priori. The autowave solution of problem (33)–(36) is defined by a value $\omega < 1$ for which the separatrix entering the singular point $(\theta_\infty, z_e(\theta_\infty))$ passes through the origin (strictly speaking, near the origin). For semitrajectories (in the range $r_0 \leqslant r < +\infty$; $0 \leqslant \theta < \theta_\infty$), the values of σ and P are found from Eqns (63), (64), and (66). The calculated profiles of the dimensionless temperature and distribution functions σ in the space–time variable are presented in Fig. 12. At low temperatures θ_∞, the semitrajectories pass near the origin, and the boundary condition at $r \to -\infty$ is only approximately satisfied. A further rise in the temperature results in the semitrajectories passing far from the origin.

The distribution functions of σ, σ_q, and σ_{ch} in r have a well-pronounced peak for all trajectories (Fig. 13). As θ_∞ decreases, the trajectories shift to a lower temperature range, while the σ, σ_q, and σ_{ch} values (including maximum ones) also become smaller at each r. At the same time, numerical simulation has demonstrated that the total entropy production in the system calculated from Eqn (64) for the ranges $(r_0, r \to +\infty)$ or $(r \to -\infty, r \to +\infty)$ under the condition $K(\theta) = 0$ at $\theta \leqslant \varepsilon_\theta$ is a functional of the autowave solution. Figure 14 illustrates the extremal character of the dependence $P(\theta_\infty)$. The minimum of P corresponds to a single trajectory for which reactant concentrations practically reach the input values $(z = 0)$ at higher temperatures $(\theta > 0)$ than the temperature at the entry to the catalyst bed (curve *2* in Fig. 14 corresponds to curves *2* in Fig. 9 and

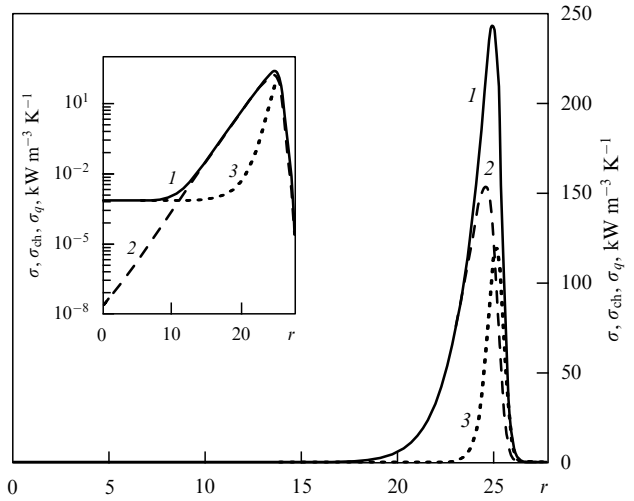

Figure 13. Distribution function of the local entropy production in the space–time variable for a trajectory of system (33), (34) at $\theta_\infty = 65.98$: curve *1* — total value (corresponds to curve *1′* in Fig. 12), curve *2* — contribution of heat conduction, curve *3* — contribution of chemical reactions.

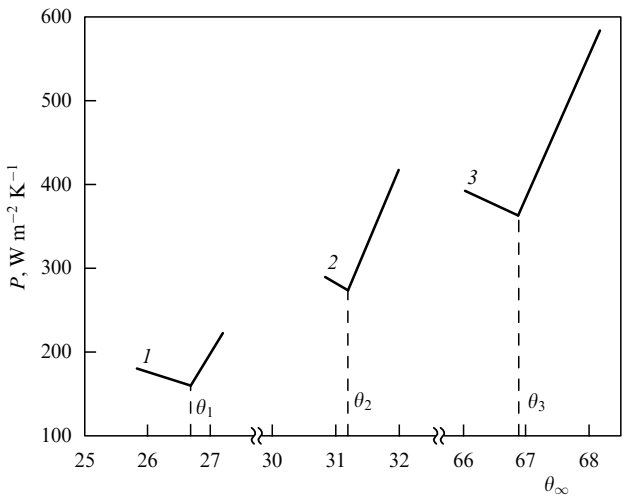

Figure 14. Total entropy production plotted versus the dimensionless temperature at plus infinity: line *1* — $T_0 = 400$ K, $u = 0.3$ m s^{-1}, $\theta_1 = 26.73$ ($\omega_1 = -0.266$; line *2* — $T_0 = 400$ K, $u = 1$ m s^{-1}, $\theta_2 = 31.21$ ($\omega_2 = 0.4338$); line *3* — $T_0 = 300$ K, $u = 1$ m s^{-1}, $\theta_3 = 66.84$ ($\omega_3 = 0.538$).

Fig. 12). We note that in the numerical search for minimal P, the temperature near the extremum was varied to within 0.001 K.

The cause of nonmonotonic dependence of the functional $P(\theta_\infty)$ can be elucidated by differential analysis of distribution functions in r of the local entropy production due to the chemical reaction and heat conduction. With increasing the temperature θ_∞ at plus infinity, the trajectories of system (33), (34) pass into a higher temperature region (see Fig. 9), and the local entropy production in the domain of intense processes grows by virtue of both chemical reaction and heat conduction (see Fig. 12). Therefore, the functional P also increases. Figure 12 shows that the temperature gradient decreases upon lowering the temperature along the space–time coordinate r; this results in a significantly smaller σ_q

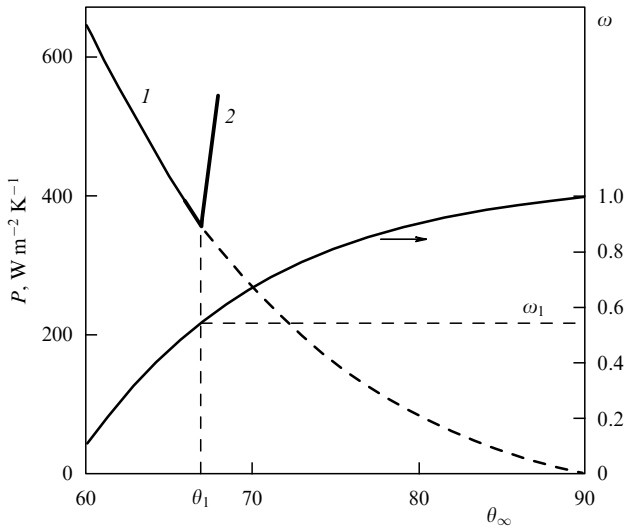

Figure 15. Dependence of the total entropy production and dimensionless propagation velocity on the dimensionless temperature at plus infinity at the gas filtration rate $u = 1$ m s^{-1} and $T_0 = 300$ K: line *1* — calculation from formula (66); line *2* — calculation from formula (64); $\theta_1 = 66.84$; $\omega_1 = 0.538$.

(curve *2*). At the same time, σ_{ch} depends only on the local reactant concentrations and temperatures but not on their gradients. When trajectories of the solutions reach the heat balance null isocline at $z > 0$ (curves *1* in Figs 9 and 12), the 'time' r_0 needed to achieve the input concentrations and temperatures substantially increases (the reaction domain broadens). For this reason, the total entropy production P in the system also increases as an integral quantity. The intersection point of the dependences $P(\theta_\infty)$ of different characters defines the functional minimum and corresponds to the physically meaningful solution of the problem, i.e., SHWs.

Interestingly, those trajectories of solutions of system (33), (34) that leave the physical domain of the phase space and do not satisfy the boundary conditions or those that approach the heat balance null isocline at $z > 0$ (curves *1* and *3* in Figs 9 and 12) are not devoid of physical interpretation. Each of them may represent a physically meaningful solution of the problem with different boundary values corresponding to a point on the heat balance null isocline approximated by a phase trajectory of system (33), (34) moving horizontally.

The total entropy production $P(\theta_\infty)$ can be calculated in accordance with (66) in a wide range of the temperatures θ_∞. However, such a calculation makes sense only for semitrajectories passing close to the origin, i.e., in a certain temperature range that is, generally speaking, unknown in advance. Formula (66) describes the left branch of dependence 2 alone (curve *1* in Fig. 15). It follows from Fig. 15 that this dependence is nonlinear and the function $P(\theta_\infty)$ decreases smoothly with increasing temperature. Figure 15 also illustrates the calculation of $\omega(\theta_\infty)$ using formula (39) and shows that a physically meaningful solution of the problem has the largest front propagation velocity among all mathematically equivalent autowave solutions.

Curiously enough, solutions with minimal wave velocity are stable in the Kolmogorov–Petrovskiĭ–Piskunov theory of the spread of epidemics and 'genes' [1, 2, 32] and in the theory of laminar flame propagation [174–176].

The results obtained allow the variational problem for SHW calculation to be formulated as follows:

$$\frac{\mathrm{d}\theta}{\mathrm{d}r} = (1-\omega)\theta - (1-\alpha\omega)Qz\,,$$

$$\frac{\mathrm{d}z}{\mathrm{d}r} = \frac{K(\theta)\big(z_{\mathrm{e}}(\theta)-z\big)}{1-\alpha\omega}\,,$$

$$P = \rho_{\mathrm{g}} u c_p \int_{-\infty}^{+\infty} \left[K(\theta)\big(z_{\mathrm{e}}(\theta)-z\big)\frac{RC_0}{\rho_{\mathrm{g}} c_p} \ln \frac{K_p(\theta)(z_{\mathrm{A},0}-z)}{1-z_{\mathrm{A},0}+z} + \left(\beta\,\frac{(1-\omega)\theta-(1-\alpha\omega)Qz}{1+\beta\theta}\right)^2\right] \mathrm{d}r \to \min\,,$$

$$r\to-\infty:\quad \theta\to 0\,,\quad z\to 0\,,$$

$$r\to+\infty:\quad \theta\to\theta_\infty\,,\quad z\to z_{\mathrm{e}}(\theta_\infty)\,.$$

It has a solution under additional, easily programmed conditions, that is, when the reaction rate constant vanishes in the small vicinity of the input temperature, $K(\theta)=0$ at $\theta \leqslant \varepsilon_\theta$, and trajectories that leave the physical domain of the phase space ($z<0$) at $\theta>\varepsilon_\theta$ are disregarded.

As the temperature at the input of the catalyst bed rises from $T_0 = 300$ K to $T_0 = 400$ K, the maximum temperature in SHWs decreases along with a decrease in the total entropy production in the system (P) and front propagation velocity (see Fig. 14). The on-coming motion of an SHW can be observed at low linear velocities of the gas (see Fig. 10) [58, 71]. By way of example, if the linear gas velocity is $u = 0.3$ m s^{-1}, the SHW propagates counter to the gas flow with the velocity $\omega_1 = -0.266$ ($V_{\mathrm{f},1} = -0.114$ mm s^{-1}); if the gas flows with the velocity $u = 1$ m s^{-1}, the SHW travels in the direction of gas filtration with the velocity $\omega_2 = 0.4338$ ($V_{\mathrm{f},2} = 0.619$ mm s^{-1}) (Fig. 16). Autowaves propagating with and against the gas flow are characteristically different in several respects. The on-coming motion of autowaves is associated with steeper temperature and concentration gradients in the wave front, maximum temperatures below the temperature of adiabatic heating of the reaction mixture, and larger degrees of the initial reagent transformation (heat released in the course of the chemical reaction is utilized to warm up a cold portion of the catalyst bed). Also, local and total entropy production in the system decreases (see Figs 14 and 16). We note that an enhancement of the degree of reagent transformation is accompanied by a decrease in the overall productivity of the process caused by the lowered gas filtration rate (smaller amount of material available for the reaction).

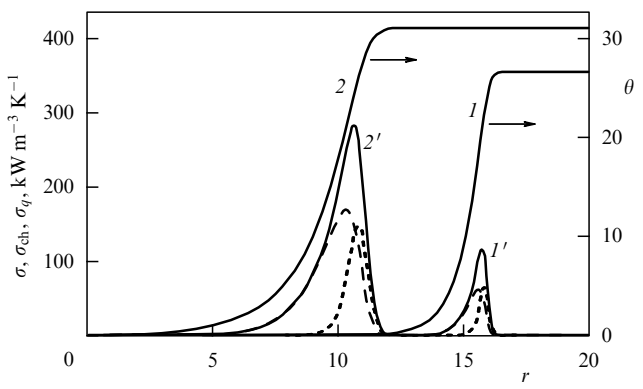

Figure 16. Profiles of the dimensionless temperature and distribution functions σ (solid lines), σ_q (dashed lines), and σ_{ch} (dotted lines) in the space–time variable of SHWs at $T_0 = 400$ K: curve *1* — $u = 0.3$ m s^{-1}, $\theta_1 = 26.73$ ($\omega_1 = -0.266$); curve *2* — $u = 1$ m s^{-1}, $\theta_2 = 31.21$ ($\omega_2 = 0.4338$).

The main conclusions at the end of this section can be formulated as follows.

We have constructed the entropy balance equation in the approximation of the quasi-homogeneous model for a static catalyst bed involved in a reversible chemical reaction proceeding by the simplest mechanism. Distribution functions of local entropy production in the space–time variable have been analyzed and mechanisms of the total entropy production in FHWs and SHWs investigated. It is shown that for mathematically equivalent solutions of the SHW propagation problem, the total entropy production in the system is a functional with extremal properties. The functional minimum corresponds to the sole physically plausible solution of the problem, i.e., an SHW propagating with the maximum possible velocity. The Arrhenius (nonlinear) law of the chemical reaction rate imposes no constraints on the principle of minimum total entropy production in a broad temperature range.

4. Nonequilibrium thermodynamics of sulfur dioxide oxidation autowaves

4.1 Mathematical formulation of the problem

A quasi-homogeneous model of nonstationary processes in a reactor with a static catalyst bed for sulfur dioxide oxidation $SO_2 + 0.5\,O_2 = SO_3$ in the presence of an inert gas is given by [175]

$$(\varepsilon_{\mathrm{g}}\rho_{\mathrm{g}} c_p + \varepsilon_{\mathrm{c}}\rho_{\mathrm{c}} c_{\mathrm{c}})\frac{\partial T}{\partial t} = \lambda\frac{\partial^2 T}{\partial \ell^2} - \rho_{\mathrm{g}} u c_p \frac{\partial T}{\partial \ell} + \frac{q}{M_{\mathrm{S}}}\,v(T,p_i)\,, \tag{67}$$

$$\varepsilon_{\mathrm{g}}\rho_{\mathrm{g}}\frac{\partial y_i}{\partial t} = -\rho_{\mathrm{g}} u\frac{\partial y_i}{\partial \ell} - \chi_i\frac{M_i}{M_{\mathrm{S}}}\,v(T,p_i)\,,\qquad i=1,\ldots,4\,, \tag{68}$$

$$p = \rho_{\mathrm{g}} RT\sum_{i=1}^{4}\frac{y_i}{M_i} \tag{69}$$

with the boundary conditions

$$\ell = \frac{-L}{2}:\quad \lambda\frac{\partial T}{\partial \ell} = \rho_{\mathrm{g}} u c_p (T-T_0)\,,\quad y_i = y_{i,0}\,,\quad i=1,\ldots,4\,, \tag{70}$$

$$\ell = \frac{+L}{2}:\quad \lambda\frac{\partial T}{\partial \ell} = 0\,, \tag{71}$$

and the initial conditions

$$t=0:\quad T(0,\ell) = T_n\,,\quad y_i(0,\ell) = y_{i,n}\,,\quad i=1,\ldots,4\,.$$

Here, $u = \sum_i \rho_i u_i/\rho_{\mathrm{g}}$ is the mass-averaged velocity of the flux of reactants per total cross section of the catalyst bed; y_{S} and $y_i = \rho_i/\rho_{\mathrm{g}}$ are mass fractions of sulfur dioxide and the ith component; q is the heating effect of the reaction per mole SO_2; M_{S} and M_i are the molecular weights of sulfur dioxide and the ith component, respectively; p and p_i are the total and partial pressure of the ith component of the reaction mixture; v is the sulfur dioxide oxidation rate expressed in mass units;

and

$$\sum_{i=1}^{n} \chi_i M_i = 0 .$$

The model assumes that the reaction mixture satisfies the ideal gas law. A gas flow with a negligibly small pressure gradient is then considered. Writing the mass and energy balance equations in terms of component mass densities rather than molar concentrations makes it easy to take into account possible changes in the gas flow rate upon variations of the number of moles in the course of the reaction.

The rate of sulfur dioxide oxidation (under the assumption that it is a missing component) is described by the Boreskov – Ivanov equation [193]

$$v(T,x) = k_0 \exp\left(-\frac{E}{RT}\right) \frac{1-x}{1-0.2x} \times \left[p\,\frac{b-0.5ax}{1-0.5ax} - \left(\frac{x}{(1-x)\,K_p(T)}\right)^2\right], \quad (72)$$

where

$$x = \frac{pa - p_{\mathrm{S}}}{pa - 0.5ap_{\mathrm{S}}}$$

is the degree of sulfur dioxide transformation, a and b are the respective mole fractions of sulfur dioxide and oxygen in the reaction mixture, and p_{S} is the partial pressure of sulfur dioxide.

We note that empirical equation (72) is an approximate one and at variance with current views of the reaction mechanism that accounts for the process of slow crystallization of vanadium from a melt of the active component [194]. The possibility of using this equation to calculate steady-state regimes of reactors under atmospheric pressure has been confirmed by experience with its practical application for many years now. Experimentally found parameters of reactor performance with a periodically reversed gas flow were compared with calculations based on Eqn (72) and a kinetic equation taking crystallization of the active component into account [194]. The results showed that Eqn (72) can be used to evaluate characteristics of the reverse process.

Summation of Eqns (68) over i from 1 to 4 leads to continuity equation (2). If the solution of the 'traveling wave' type exists, it must satisfy a stationary problem in the system of coordinates moving with the front. Bearing in mind that the degree of dioxide transformation is easily found via mass fractions, $x = (y_{\mathrm{S},0} - y_{\mathrm{S}})/y_{\mathrm{S},0}$, problem (67) – (71), with (72), takes the form

$$\frac{\mathrm{d}\theta}{\mathrm{d}r} = (1-\omega)\theta - (1-\alpha\omega)Q_{\mathrm{S}}x\,, \quad (73)$$

$$\frac{\mathrm{d}x}{\mathrm{d}r} = \frac{K(\theta)(1-x)}{(1-\alpha\omega)(1-0.2x)}\left[p\,\frac{b-0.5ax}{1-0.5ax} - \left(\frac{x}{K_p(\theta)(1-x)}\right)^2\right], \quad (74)$$

$$r \to -\infty: \quad \theta \to 0\,, \quad x \to 0\,, \quad (75)$$

$$r \to +\infty: \quad \theta \to \theta_\infty\,, \quad x \to x_{\mathrm{e}}(\theta_\infty)\,. \quad (76)$$

Here,

$$K(\theta) = \frac{k_0\lambda}{c_p\,y_{\mathrm{S},0}(\rho_{\mathrm{g}}u)^2} \exp\left(-\frac{1}{\beta}\right) \exp\left(\frac{\theta}{1+\beta\theta}\right),$$

$$Q_{\mathrm{S}} = \frac{q y_{\mathrm{S},0}}{M_{\mathrm{S}} c_p \beta T_0}\,,$$

and $x_{\mathrm{e}}(\theta)$ is the equilibrium degree of transformation corresponding to the dimensionless temperature θ.

As pointed out above, the continuity equation in a moving frame of coordinates yields $\rho_{\mathrm{g}}(u - \varepsilon_{\mathrm{g}}V_{\mathrm{f}}) = \text{const}$. Hence, there is reason to consider ρ_{g} and u as given under the input conditions.

We recall that if the reagent concentrations at the input of the catalyst bed do not satisfy the conditions of a thermodynamically equilibrated reaction, only SHWs can propagate in the catalyst bed. In other words, problem (73) – (76) has solutions only at $\omega < 1$. In this problem, neither the SHW propagation velocity nor the temperature at plus infinity is known. For the trajectory to come to the stationary point at $r \to +\infty$ in accordance with condition (76), the parameters ω and θ_∞ must be related by the integral energy balance equation

$$\omega = \frac{\theta_\infty - Q_{\mathrm{S}}x_{\mathrm{e}}(\theta_\infty)}{\theta_\infty - \alpha Q_{\mathrm{S}}x_{\mathrm{e}}(\theta_\infty)}\,. \quad (77)$$

Therefore, problem (73) – (76) contains only one parameter, either ω or θ_∞; that is, it can have a one-parameter family of solutions satisfying the boundary conditions.

Autowave solutions of the system of two ordinary differential equations (73), (74) correspond on the phase plane (θ, x) to a trajectory connecting two singular (stationary) points. One of them, defined by the conditions at $r \to -\infty$, is located at the intersection of the null isocline of Eqn (74), $T = 0$ K, with the null isocline of Eqn (73), $x = (1-\omega)\theta/((1-\alpha\omega)Q_{\mathrm{S}})$ (heat balance null isocline). This singular point is a complex equilibrium state; the matrix of the system linearized in its vicinity has zero and positive eigenvalues. The second singular point defined by the conditions at $r \to +\infty$ is a saddle; it is actually the intersection point of the null isocline of Eqn (73) and the null isocline $x = x_{\mathrm{e}}(\theta)$, i.e., the thermodynamic equilibrium curve. This implies that the only solution of the problem in this case is the saddle separatrix.

4.2 Local entropy production in an autowave

Heat balance equation (67), frequently obtained by independent considerations, is the equivalent to enthalpy balance equation (4). For autowave solutions of the problem in a system of coordinates associated with the propagating front, the enthalpy balance is described by ordinary differential equation (57). By substituting (57) in Gibbs equation (52) and eliminating the derivatives of component concentrations with the help of Eqn (74), we obtain the entropy balance equation

$$\frac{\rho_{\mathrm{g}}c_p u}{\lambda}\frac{\mathrm{d}}{\mathrm{d}r}\left((1-\alpha\omega)\,\rho_{\mathrm{g}}us_{\mathrm{g}} - \frac{\omega}{\gamma}\,u\varepsilon_{\mathrm{c}}\,\rho_{\mathrm{c}}s_{\mathrm{c}} + \rho_{\mathrm{g}}uc_pT\,\frac{\mathrm{d}(1/T)}{\mathrm{d}r}\right) = \frac{Av(T,x)}{TM_{\mathrm{S}}} + \frac{(\rho_{\mathrm{g}}uc_p)^2}{\lambda}\,T^2\left(\frac{\mathrm{d}(1/T)}{\mathrm{d}r}\right)^2, \quad (78)$$

where

$$A = RT \ln\left(\frac{K_p(T)(1-x)\big(p(b-0.5ax)\big)^{1/2}}{x(1-0.5ax)^{1/2}}\right)$$

is the chemical affinity of the sulfur dioxide oxidation reaction.

The right-hand side of Eqn (78) is the local entropy production in the system, constituted by two terms:

$$\sigma = \frac{Av(T,x)}{TM_{\mathrm{S}}} + \frac{(\rho_{\mathrm{g}} u c_p)^2}{\lambda} T^2 \left(\frac{\mathrm{d}(1/T)}{\mathrm{d}r}\right)^2 = \sigma_{\mathrm{ch}} + \sigma_q \geqslant 0\,. \tag{79}$$

The first one (σ_{ch}) accounts for the local entropy production resulting from chemical reaction and the second (σ_q) for the local entropy production due to heat conduction. In agreement with the second law of thermodynamics, σ_{ch} and σ_q must be positive definite quantities. With (73), expression (79) acquires the form

$$\sigma = \frac{(\rho_{\mathrm{g}} u c_p)^2}{\lambda}\left\{\frac{R}{M_{\mathrm{S}} c_p} \ln\left(\frac{K_p(\theta)(1-x)\big(p(b-0.5ax)\big)^{1/2}}{x(1-0.5ax)^{1/2}}\right)\right.$$
$$\times K(\theta)\frac{1-x}{1-0.2x}\left[p\,\frac{b-0.5ax}{1-0.5ax} - \left(\frac{x}{K_p(\theta)(1-x)}\right)^2\right]$$
$$\left. + \left(\beta\,\frac{(1-\omega)\theta - (1-\alpha\omega)Q_{\mathrm{S}} x}{1+\beta\theta}\right)^2\right\} \tag{80}$$

in dimensionless variables.

We recall that thermodynamic forces and flows vanish ($v = 0$, $A = 0$, $J_q = 0$, $X_q = 0$) at equilibrium points of dynamic system (73), (74), i.e., at the intersection points of null isoclines. That $\sigma_{\mathrm{ch}} \to 0$ at $T \to 0$ K is easy to verify by finding the corresponding limit

$$\lim_{T\to 0} \frac{Av(T,x)}{TM_{\mathrm{S}}}$$
$$= \lim_{T\to 0} \frac{R}{M_{\mathrm{S}}} \ln\left(k_{\mathrm{e}} \exp\left(\frac{q}{RT}\right)\frac{(1-x)\big(p(b-0.5ax)\big)^{1/2}}{x(1-0.5ax)^{1/2}}\right)$$
$$\times k_0 \exp\left(-\frac{E}{RT}\right)\frac{1-x}{1-0.2x}$$
$$\times \left[p\,\frac{b-0.5ax}{1-0.5ax} - \left(\frac{x}{(1-x)k_{\mathrm{e}}\exp\big(q/(RT)\big)}\right)^2\right] = 0\,.$$

Hence, the local entropy production at $r \to \pm\infty$ tends to zero: $\sigma \to 0$.

4.3 The principle of minimum total entropy production in autowave processes of sulfur dioxide oxidation

The total entropy production P in SHWs for the one-dimensional problem in (73)–(76) is an integral of expression (80) over the space–time coordinate:

$$P = \rho_{\mathrm{g}} u c_p \int_{-\infty}^{+\infty}\left\{\frac{R}{M_{\mathrm{S}} c_p} \ln\left(\frac{K_p(\theta)(1-x)\big(p(b-0.5ax)\big)^{1/2}}{x(1-0.5ax)^{1/2}}\right)\right.$$
$$\times K(\theta)\frac{1-x}{1-0.2x}\left[p\,\frac{b-0.5ax}{1-0.5ax} - \left(\frac{x}{K_p(\theta)(1-x)}\right)^2\right]$$
$$\left. + \left(\beta\,\frac{(1-\omega)\theta - (1-\alpha\omega)Q_{\mathrm{S}} x}{1+\beta\theta}\right)^2\right\}\mathrm{d}r\,. \tag{81}$$

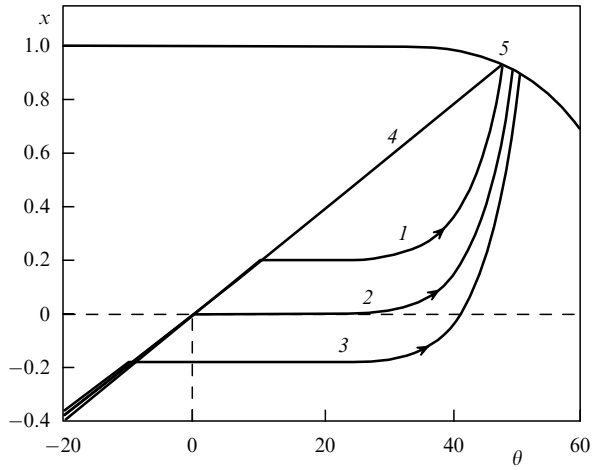

Figure 17. Trajectories of system of equations (73), (74) on the phase plane at dimensionless temperatures on plus infinity: curve *1* — $\theta_\infty = 47.38$, curve *2* — $\theta_\infty = 48.84$, curve *3* — $\theta_\infty = 49.88$, *4* — heat balance null isocline for the trajectory represented by curve *1*, *5* — thermodynamic equilibrium curve.

Because autowave (bounded) solutions of the problem are sought in the class of smooth bounded functions and σ is a positive definite bounded function, the total entropy production P in the system is also a positive definite bounded function. The problem of SHW propagation is known to have no analytic solutions; the temperature θ_∞ at $r \to +\infty$ is not known in advance. Therefore, we numerically study the patterns of local and total entropy production in the course of sulfur dioxide oxidation.

For an arbitrarily chosen value of θ_∞ [with $x_{\mathrm{e}}(\theta_\infty)$ and ω found from Eqn (77)], it is possible to numerically construct a separatrix trajectory entering the equilibrium point $(\theta_\infty, x_{\mathrm{e}}(\theta_\infty))$ by integration of the system of equations (73), (74) in the direction opposite to that of the vector field (over the 'inverse time'). Our calculations were made at the following characteristic values of parameters [175, 194]:

$$T_0 = 333.15\ \mathrm{K};\quad p = 0.1\ \mathrm{MPa};\quad a = 0.2;\quad b = 0.3;$$
$$c_{\mathrm{c}} = 1255.2\ \mathrm{J\,kg^{-1}\,K^{-1}};\quad c_p = 911\ \mathrm{J\,kg^{-1}\,K^{-1}};$$
$$u = 0.1\ \mathrm{m\,s^{-1}};\quad q = 97.3\ \mathrm{kJ\,mol^{-1}};$$
$$k_0 = 9.2\times 10^6\ \mathrm{kg\,m^{-3}\,s^{-1}\,MPa^{-1}};$$
$$k_{\mathrm{e}} = 1.476\times 10^{-4}\ \mathrm{MPa^{-1/2}};$$
$$\varepsilon = 0.41;\quad \varepsilon_{\mathrm{p}} = 0.3;\quad \lambda = 14.64\ \mathrm{W\,m^{-1}\,K^{-1}};$$
$$\rho_{\mathrm{g}} = 1.62\ \mathrm{kg\,m^{-3}};\quad \rho_{\mathrm{c}} = 1570\ \mathrm{kg\,m^{-3}}\,.$$

The activation energy in Eqn (72) is temperature-dependent [193, 194]. For simplicity, we assume that $E = 92.05\ \mathrm{kJ\,mol^{-1}}$.

Figure 17 shows trajectories of system (73), (74) on the phase plane (θ, x). Numerical simulation has demonstrated that trajectories arising at sufficiently high temperatures θ_∞ leave the physical domain of the phase space far from the corresponding heat balance null isoclines and then come closer to their own null isoclines in the region of negative degrees of transformation (curve *3* in Fig. 17). Such trajectories must be disregarded because the reactant concentrations do not take negative values. Other trajectories originating at sufficiently low temperatures θ_∞ reach their

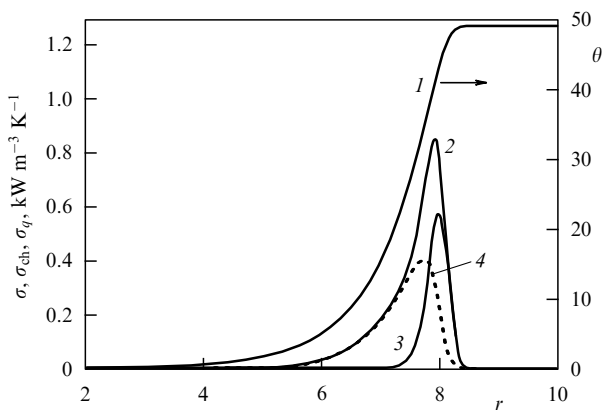

Figure 18. Profiles of the dimensionless temperature (curve *1*) and distribution functions of the local entropy production (curve *2*) in the space–time coordinate of a sulfur dioxide oxidation autowave at the dimensionless temperature at plus infinity $\theta_\infty = 48.84$ (corresponds to curve *2* in Fig. 17); *3* — contribution of chemical reaction; *4* — contribution of heat conduction.

null isoclines at $\theta > 0$ and $x > 0$, then move in their vicinity, and finally reach the neighborhood of the point $(0, 0)$ for a finite (even if rather large) 'time' r_0. For curve *1* with the heat balance null isocline *4* (see Fig. 17), the 'time' $r_0 \approx 1.3 \times 10^6$. If $T_0 \neq 0$ K, the point at $r \to -\infty$ is not stationary $(v(T_0, x) \neq 0)$ and trajectories coming very close to the null isoclines pass near the point $(0, 0)$, appear in the region of $x < 0$, and eventually reach the singular point at $\theta = -1/\beta$ $(T = 0$ K). Strictly speaking, the problem posed has no solution.

It is worth noting that separatrix trajectories cannot cross null isoclines; this follows from the analysis of the system's vector field. At low temperatures, the chemical reaction rate may fall; therefore, all separatrix trajectories at low temperatures are characterized by the following behavior of the image point. If this point is located far from the heat balance null isocline, it 'rapidly' approaches the null isocline and thereafter moves 'slowly' near the null isocline towards low temperatures. At $x = 0$, the deviation of the dimensionless temperature from zero for these semitrajectories is small $(\varepsilon_\theta \approx 10^{-6})$. If the reaction rate is artificially set equal to zero near the point $(0, 0)$ (at $\theta < \varepsilon_\theta$), the output conditions at $r \to -\infty$ correspond to the equilibrium state (singular point) of system (73), (74) and the problem has solutions. But this does not suffice for choosing the sole physically meaningful solution of the problem from the family of mathematically equivalent solutions.

There is only one semitrajectory that horizontally approaches the heat balance null isocline at $x = 0$ (curve *2* in Fig. 17). To find this sole semitrajectory, it is necessary to nullify ('cut off') the reaction rate at temperatures higher than the input temperature and to demonstrate that the sought solution of the problem is independent of the cut-off temperature in a wide range of its values.

For all semitrajectories, Eqns (80) and (81) were used to calculate the distribution functions of local entropy production in r and the total entropy production P in the system. Figure 18 gives an example of the calculated profiles of the temperature and distribution functions of σ, σ_q, and σ_{ch} in r for the sole physically meaningful solution of the problem. The distribution functions of σ, σ_q, and σ_{ch} in r have distinct maxima for all mathematically equivalent semitrajectories. As θ_∞ decreases, these functions and their maximum values also decrease at each point r.

We note that the analysis of the distribution function of σ_{ch} in r leads to the conclusion that the bulk of sulfur dioxide undergoes transformation at high temperatures in a narrow reaction zone near thermodynamic equilibrium of the reaction. This accounts for even less strict requirements as regards the accuracy of the description of sulfur dioxide oxidation kinetics in the simulation of autowave processes than in modeling stationary processes.

Numerical simulation has demonstrated that the total entropy production P calculated for the ranges $(r_0,\ r \to +\infty)$ and $(r \to -\infty,\ r \to +\infty)$ under the condition of the reaction rate vanishing near $(0, 0)$ $(v(\theta, x) = 0$ at $\theta < \varepsilon_\theta,\ x = 0)$ is a functional of the autowave solution. The functional minimum corresponds to a single semitrajectory that satisfies the cut-off procedure for the reaction rate at low temperatures. We note that in the numerical search for minimal $P(\theta_\infty)$, the temperature near the extremum was varied to within 10^{-4} degree.

Extremal properties of the functional $P(\theta_\infty)$ are attributable to the difference between integral contributions from σ_q and σ_{ch}. A fall in the temperature results in a sharp decrease in the heat released by virtue of the proceeding chemical reaction. The temperature gradient in r also decreases such that the maximum and current values of σ_q may differ by a factor of 10^7. We note that the value of σ_{ch} in the vicinity of the heat balance null isocline is approximately 10^4 times that of σ_q. Therefore, the integral contribution of σ_{ch} for trajectories approaching null isoclines at $\theta > 0$ and $x > 0$ increases: the longer the path parallel to the null isocline, the greater the increase. As a result, the functional P grows.

Thus, the results obtained permit us to formulate the following variational problem for the computation of SHWs generated as a result of sulfur dioxide oxidation:

$$\frac{\mathrm{d}\theta}{\mathrm{d}r} = (1-\omega)\theta - (1-\alpha\omega)Q_{\mathrm{S}}x\,,$$

$$\frac{\mathrm{d}x}{\mathrm{d}r} = \frac{K(\theta)(1-x)}{(1-\alpha\omega)(1-0.2x)}\left[p\,\frac{b-0.5ax}{1-0.5ax} - \left(\frac{x}{K_p(\theta)(1-x)}\right)^2\right],$$

$$P = \rho_{\mathrm{g}} u c_p \int_{-\infty}^{+\infty}\left\{\frac{R}{M_{\mathrm{S}}c_p}\ln\left(\frac{K_p(\theta)(1-x)\big(p(b-0.5ax)\big)^{1/2}}{x(1-0.5ax)^{1/2}}\right)\right.$$
$$\times K(\theta)\frac{1-x}{1-0.2x}\left[p\,\frac{b-0.5ax}{1-0.5ax} - \left(\frac{x}{K_p(\theta)(1-x)}\right)^2\right]$$
$$\left. + \left(\beta\,\frac{(1-\omega)\theta - (1-\alpha\omega)Q_{\mathrm{S}}x}{1+\beta\theta}\right)^2\right\}\mathrm{d}r \to \min\,,$$

$$r \to -\infty\colon\quad \theta \to 0\,,\quad x \to 0\,;$$

$$r \to +\infty\colon\quad \theta \to \theta_\infty\,,\quad x \to x_{\mathrm{e}}(\theta_\infty)\,.$$

This problem is solvable under additional, easily programmed conditions, that is, when the reaction rate constant vanishes in the small vicinity of input temperature values, $K(\theta) = 0$ at $\theta < \varepsilon_\theta$, and solutions leaving the physical domain of the phase space $(x < 0)$ at $\theta > \varepsilon_\theta$ are disregarded.

The propagation velocity of an SHW is one of its main characteristics. Interestingly, a rise in the gas filtration rate may result in a change in SHW direction. Figure 18 shows an SHW that slowly travels counter to the gas flow $(\omega = -0.0964,\ V_{\mathrm{f}} = -1.75 \times 10^{-5}$ m s^{-1}, $u = 0.1$ m s^{-1}). The degree of sulfur dioxide transformation is $x = 0.914$. With increasing the linear gas filtration rate, the SHW propagates in the direction of gas filtration. For example,

the front velocity $V_f = 0.45 \times 10^{-5}$ m s^{-1} ($\omega = 0.0177$) at the linear filtration rate $u = 0.14$ m s^{-1}. At the same time, the maximum temperature and total entropy production in the system increase and the degree of sulfur dioxide transformation decreases: $x = 0.868$. We note that there is only one solution with $\omega = 0$, i.e., a 'standing' SHW, in the approximation of the quasi-homogeneous model of a static catalyst bed.

To conclude this section, we note that simulation of a real industrial-scale AWP of sulfur dioxide oxidation has been used to illustrate the constructive, positive role of the thermodynamics of irreversible processes. It was shown that the nonlinear mechanism of chemical transformation of sulfur dioxide imposes no constraints on the principle of minimum total entropy production in a wide temperature range.

5. Conclusion

The results in the present review prove convincingly that the combination of methods of nonequilibrium thermodynamics and AWP theory affords a deeper insight into the physical nature of autowave phenomena. Investigations into SHW propagation by the qualitative analysis of a quasi-homogeneous model of a static catalyst bed without introducing any additional assumptions have demonstrated the existence of a one-parameter family of phase trajectories connecting singular (stationary) points of the dynamical system. The derivation of the concrete form of the entropy balance equation for a system with propagating SHWs, as well as its qualitative and numerical analysis, has made it possible to establish the principle of maximum total entropy production in the system and offer a variational formulation of the problem. The extension of variational principles of nonequilibrium thermodynamics to SHWs may be considered a thermodynamic substantiation of the artificial cut-off procedure for the reaction rate (setting it equal to zero) at low temperatures.

It is appropriate to note that the total entropy production (increase in entropy) may be taken as the Lyapunov function, which has the properties of a potential. With the transient wave processes disregarded, one can only speak about autowave resistance to perturbations of the parameters of the systems. Because fluctuations of the parameters have no apparent effect on the qualitative behavior of the system, the autowaves are structurally stable. The Arrhenius (nonlinear) law of chemical reaction and nonlinearity of the reaction mechanism impose no constraints on the principle of minimum total entropy production in a wide temperature range. It is important to emphasize that extremal principles of nonequilibrium thermodynamics are essentially equivalent [142 – 145, 160]. At the same time, the form of representation of the variational principle proves to be of paramount importance for the solution of specific problems.

Various profound analogies between autowaves generated in a static catalyst bed and laminar combustion autowaves promoted successful application of nonequilibrium thermodynamics methods to the theory of combustion [170 – 172]. The discussion of these works is beyond the scope of the present review. Nevertheless, the very fact that the methodology of nonlinear thermodynamics is used for the purposes of combustion theory indicates the fruitfulness of this approach. We note that Ref. [172] reports a study of a dynamical system with the three-dimensional phase space, i.e., the problem of propagation of laminar combustion autowaves at an arbitrary Louis number. So far, we have considered only dynamical systems with the two-dimensional phase space.

The existence of a space – time dissipative structure (FHW) 'near' the system's thermodynamic equilibrium is of philosophical interest. It was shown earlier in this review that an FHW theoretically appears at any nonzero dimensionless temperature θ_∞, but the front extends to infinity at $\theta_\infty \to 0$, i.e., the FHW degenerates. That FHW propagation is possible only in a reversible chemical reaction has only been inferred from theoretical studies [67 – 70].

It is worth noting that all arguments developed and the results presented in this review do not go beyond the framework of the second principle of thermodynamics. The entropy balance equation was constructed in terms of the basic assumptions of a mathematical model: first idealization of the phenomenon, then joint application of the methods of nonequilibrium thermodynamics and AWP theory in the framework of the adopted idealization. Variational principles of nonequilibrium thermodynamics in the AWP science appear to be of fundamental importance in expanding our knowledge of the nature of autowave phenomena.

I conclude this review by a well-known formulation of the principle of extremum: "Light traveling between two points seeks a path such that requires a minimum time" (P Fermat, 1660).

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6. Appendix

The following lemma is true.

Lemma 1. *At $Q > 0$ and $\eta > 1$, system of equations* (33), (34) *has singular points of a saddle or node type, with a singular point (θ_s, z_s) being a saddle if and only if $f'(\theta_s) > 0$.*

The system of differential equations linearized in the vicinity of a singular point (θ_s, z_s) has the form

$$\frac{d\varkappa}{dr} = B(\theta_s, z_s)\,\varkappa\,,$$

where

$$\varkappa = \begin{bmatrix} \theta \\ z \end{bmatrix}, \qquad B = \begin{bmatrix} \varphi_\theta & \varphi_z \\ \psi_\theta & \psi_z \end{bmatrix},$$

$\varphi(\theta, z)$ is the right-hand side of Eqn (33), $\psi(\theta, z)$ is the right-hand side of Eqn (34), and φ_θ, φ_z, ψ_θ, and ψ_z are the corresponding partial derivatives.

Eigenvalues of the matrix B are real only if the discriminant $\operatorname{dis}(B)$ of the characteristic equation is nonnegative, which is true only if $Q > 0$ and $\eta > 1$ at each singular point because

$$\operatorname{dis}(B)\big|_{(\theta_s, z_s)} = \left[1 - \omega + \frac{K^0(\theta_s)}{1 - \alpha\omega}\right]^2 + \frac{4Q(\eta - 1)K(\theta_s)}{\left[1 + K_p(\theta_s)\right](1 + \beta\theta_s)^2}\,.$$

Hence, there are no fluctuations of temperature and concentrations in the neighborhood of a singular point;

these functions are monotonic. The singular point is of a saddle or node type.

By definition, a point (θ_s, z_s) is a saddle if eigenvalues of the problem linearized in its vicinity are real and have different signs. Furthermore, the determinant of the matrix B, which is equal to the product of its eigenvalues, has the form

$$D(\theta_s, z_s) = -K^0(\theta_s)\, f'(\theta_s)\,,$$

where $f(\theta)$ is found from (38). Therefore, the condition $f'(\theta_s) > 0$ implies that the signs of the eigenvalues are different. Lemma 1 is proved.

Corollary 1.1. *A singular point* (θ_s, z_s) *of system* (33), (34) *located on the thermodynamic equilibrium curve at* $Q > 0$, $\eta > 1$ *is a saddle if and only if the following inequality is satisfied*:

$$\frac{1-\omega}{1-\alpha\omega} + \frac{QK_{p,0}(\eta-1)}{\left(1+K_p(\theta_s)\right)^2(1+\beta\theta_s)^2} > 0\,.$$

This assertion follows from Lemma 1 and the formula for $z_e'(\theta_s)$. Then, it is evident that at $\omega < 1$, any point on the thermodynamic equilibrium curve is a saddle point.

Corollary 1.2. *The point* $(\theta_s, z_s) = (0,0)$ *on the thermodynamic equilibrium curve at* $Q > 0$, $\eta > 1$ *is a saddle if and only if one of the following inequalities is satisfied*:

a) $$\frac{1-\omega}{1-\alpha\omega} + \frac{QK_{p,0}(\eta-1)}{(1+K_{p,0})^2} > 0\,;$$

b) $$\frac{z_e(\theta_\infty)}{\theta_\infty} + \frac{K_{p,0}(\eta-1)}{(1+K_{p,0})^2} > 0\,;$$

c) $$\frac{\exp(-\vartheta)-1}{\theta_\infty\left(1+K_{p,0}\exp(-\vartheta)\right)} + \frac{\eta-1}{1+K_{p,0}} > 0\,,$$

where

$$\vartheta = \frac{(\eta-1)\theta_\infty}{1+\beta\theta_\infty}\,.$$

This assertion follows from Lemma 1 and Corollary 1.1.

Corollary 1.3. *At* $Q > 0$, $\eta > 1$, *the parameters* k_e, η, β, *and* θ_∞ *determine whether the singular point* $(0,0)$ *of system* (33), (34) *is a saddle if it is located on the thermodynamic equilibrium curve*.

This assertion follows directly from Corollary 1.2c).

The following lemma is true.

Lemma 2. *As* $\theta_\infty \to 0$ (*as the initial temperature of the catalyst bed approaches the input temperature*), *one of the eigenvalues of system* (33), (34) *linearized at the point* $(\theta_s, z_s) = (0,0)$ *tends to zero*.

This assertion follows from the expression for the determinant of the characteristic equation

$$D(0,0) = Qk_r\left(\frac{1-\exp(-\vartheta)}{\theta_\infty\left(1+K_{p,0}\exp(-\vartheta)\right)} - \frac{\eta-1}{1+K_{p,0}}\right)$$

and the relation $\lim_{\theta_\infty \to 0} D = 0$.

Corollary 2.1. *As* $\theta_\infty \to 0$, *the temperature and concentration profiles in an FHW become increasingly gently sloping and the front width tends to infinity*.

Corollary 2.2. *The front width of an FHW increases with decreasing* k_r.

This assertion follows from the relation $\lim_{k_r \to 0} D = 0$.

Corollary 2.3. *The front width of an FHW decreases with increasing* k_r (*at* $Q > 0$, $\eta > 1$).

This assertion follows from the relation

$$\left.\frac{\partial D}{\partial K_{p,0}}\right|_{(0,0)} = Qk_r\left(-\frac{\eta-1}{(1+K_{p,0})^2} + \frac{\left(\exp(-\vartheta)-1\right)\exp(-\vartheta)}{\theta_\infty\left(1+K_{p,0}\exp(-\vartheta)\right)^2}\right).$$

The following lemma is true.

Lemma 3. *Asymptotic values of the FHW propagation velocity* ω *are given by the expressions*

$$\omega_+ = \lim_{\theta_\infty \to +\infty} \omega(\theta_\infty) = 1\,,$$

$$\omega_0 = \lim_{\theta_\infty \to 0} \omega(\theta_\infty) = \frac{(1+K_{p,0})^2 + (\eta-1)K_{p,0}Q}{(1+K_{p,0})^2 + \alpha(\eta-1)K_{p,0}Q}\,,$$

$$\omega_- = \lim_{\theta_\infty \to -1/\beta} \omega(\theta_\infty) = \frac{1+\beta Q z_{A,0}}{1+\alpha\beta Q z_{A,0}} > 1\,.$$

This assertion follows from the formulas

$$\lim_{\theta \to +\infty} K_p(\theta) = k_e\,, \qquad \lim_{\theta \to -1/\beta+0} K_p(\theta) = +\infty\,,$$

$$\lim_{\theta \to -1/\beta+0} z_e(\theta) = z_{A,0}\,, \qquad \lim_{\theta \to 0} \frac{\partial z_e(\theta)}{\partial \theta} = -\frac{\eta-1}{(1+K_{p,0})^2}\,K_{p,0}\,.$$

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