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The H-theorem for the physico-chemical kinetic equations with explicit time discretization

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HIGHLIGHTS

- The implicit time discretisation for the physico-chemical kinetics equations is considered.
- The discussed equation includes all discrete physico-chemical kinetics.
- The H-theorem for implicit time discretisation is proved.

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ABSTRACT

There is demonstrated in the present paper, that the H-theorem in the case of explicit time discretization of the physico-chemical kinetic equations, generally speaking, is not valid. We prove the H-theorem, when the system of the physico-chemical kinetic equations with explicit time discretization has the form of non-linear analogue of the Markov process with doubly stochastic matrix, and for more general cases. In these cases the proof is reduced to the proof of the H-theorem for Markov chains. The simplest discrete velocity models of the Boltzmann equation with explicit time discretization –the Carleman and Broadwell models are discussed and the H-theorem for them in the case of discrete time is proved.

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1. Introduction

The H-theorem was for the first time discussed by Boltzmann in the paper "Weitere Studien über das Wärmegleichgewicht unter Gasmolekülen" (1872) [1]. This theorem, proving the convergence of solutions of the Boltzmann equation's type to the Maxwellian distribution, Boltzmann connected with the law of increasing entropy [2].

In connection with computer simulation, the question arises about the transition to discrete time. The discrete model should inherits the properties of the original equation. Therefore, for the physico-chemical kinetics equations necessary condition for the adequacy of this discretization is the requirement of exact conservativeness (i.e., the discrete models would have all conservation laws, which were in the original equation) and the fulfillment of the H-theorem. For which discretizations in time is the H-theorem fulfilled, and when is its proof reduced to the proof of the H-theorem for Markov chains? We consider the physico-chemical kinetics equations with an explicit discretization in time for which the H-theorem is valid, and they are simpler to count on the computer unlike the case of implicit discretization in time.

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Let there is a mixture of n chemically or physically interacting substances (states) with spatially uniform concentrations. Let us denote the number of molecules of the ith substance ($i = 1, 2, \ldots, n$) by $f_i(t)$ at time t.

The general form of equations for complex physico-chemical reactions (processes) is written in the form [3–5]:

$$\frac{df_i}{dt} = \frac{1}{2} \sum_{(\boldsymbol{\alpha},\boldsymbol{\beta})\in\Im} (\beta_i - \alpha_i) \left(K^{\boldsymbol{\alpha}}_{\boldsymbol{\beta}} \mathbf{f}^{\boldsymbol{\alpha}} - K^{\boldsymbol{\beta}}_{\boldsymbol{\alpha}} \mathbf{f}^{\boldsymbol{\beta}}\right), \quad i = 1, 2, \ldots, n. \tag{1.1}$$

Here $\mathbf{f}^{\boldsymbol{\alpha}}$ designates product $\mathbf{f}^{\boldsymbol{\alpha}} = f_1^{\alpha_1} f_2^{\alpha_2} \ldots f_n^{\alpha_n}$, the sum is on some finite set $\Im$ of pairs of indices $(\boldsymbol{\alpha}, \boldsymbol{\beta})$, $\boldsymbol{\alpha} = (\alpha_1, \alpha_2, \ldots, \alpha_n)$ and $\boldsymbol{\beta} = (\beta_1, \beta_2, \ldots, \beta_n)$ –vectors with nonnegative integer components. $(\boldsymbol{\alpha}, \boldsymbol{\beta})$ corresponds to the elementary reaction or process

$$\alpha_1 S_1 + \alpha_2 S_2 + \cdots + \alpha_n S_n {\rightarrow}^{\beta}_{1} S_1 + \beta_2 S_2 + \cdots + \beta_n S_n, \quad (\boldsymbol{\alpha}, \boldsymbol{\beta}) \in \Im, \tag{1.2}$$

S_i – chemical symbols of the reactants, $K^{\boldsymbol{\alpha}}_{\boldsymbol{\beta}} \geq 0$ –the coefficients of reaction rates (constants of reactions). Coefficients α_i, β_i are the stoichiometric coefficients. Without loss of generality, we can assume that the set $\Im$ is symmetric with respect to permutations $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$. While some couples $(\boldsymbol{\alpha}, \boldsymbol{\beta})$ may correspond to the zero coefficients of reaction rates: $K^{\boldsymbol{\alpha}}_{\boldsymbol{\beta}} = 0$, when it is possible that $K^{\boldsymbol{\beta}}_{\boldsymbol{\alpha}} > 0$ (it is allowed irreversibility of reactions or processes).

In order to be clear, let us consider the example of system of the physico-chemical kinetics equations describing a single reversible reaction $AB + CD \rightarrow AD + CB$, where A, B, C, D are symbols for some atoms or different between themselves complexes of atoms, which do not change during the reaction. We have that the set $\Im$ consists of two pairs: $(\boldsymbol{\alpha}, \boldsymbol{\beta})$ and $(\boldsymbol{\beta}, \boldsymbol{\alpha})$, where $\boldsymbol{\alpha} = (1, 1, 0, 0)$, $\boldsymbol{\beta} = (0, 0, 1, 1)$. Their components have striking physical and chemical sense. The first indexes ($\alpha_1 = 1$ and $\beta_1 = 0$) correspond to the number of molecules AB participating in the reaction, the second ($\alpha_2 = 1$ and $\beta_2 = 0$) –number of molecules CD, the third and fourth ($\alpha_3 = \alpha_4 = 0$ and $\beta_3 = \beta_4 = 1$) are the number of molecules AD and CB respectively. Let us write the system of equations according to general form (1.1):

$$\frac{df_1}{dt} = (0 - 1)\left(K^{\boldsymbol{\alpha}}_{\boldsymbol{\beta}} f_1 f_2 - K^{\boldsymbol{\beta}}_{\boldsymbol{\alpha}} f_3 f_4\right),$$
$$\frac{df_2}{dt} = (0 - 1)\left(K^{\boldsymbol{\alpha}}_{\boldsymbol{\beta}} f_1 f_2 - K^{\boldsymbol{\beta}}_{\boldsymbol{\alpha}} f_3 f_4\right),$$
$$\frac{df_3}{dt} = (1 - 0)\left(K^{\boldsymbol{\alpha}}_{\boldsymbol{\beta}} f_1 f_2 - K^{\boldsymbol{\beta}}_{\boldsymbol{\alpha}} f_3 f_4\right),$$
$$\frac{df_4}{dt} = (1 - 0)\left(K^{\boldsymbol{\alpha}}_{\boldsymbol{\beta}} f_1 f_2 - K^{\boldsymbol{\beta}}_{\boldsymbol{\alpha}} f_3 f_4\right),$$

where $f_1(t), f_2(t), f_3(t), f_4(t)$ are, respectively, the concentration of molecules of substances AB, CD, AD and CB at time t, and the values of vectors $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$ is written above. There are three linear conservation laws: $f_1 + f_3 = const$, $f_2 + f_3 = const$, $f_2 + f_4 = const$. The first of them expresses the conservation law of number of atoms of the specie A: $f_1 + f_3$, the second is the number of atoms of the form D: $f_2 + f_3$, the third –the number of atoms of the specie C: $f_2 + f_4$. The conservation law of number of atoms of the form B: $f_1 + f_4$, is linear combination of the previous ones. It is easy to check that the linear invariant: $I_{\boldsymbol{\mu}}(t) = \sum_{i=1}^{n} \mu_i f_i(t) = (\boldsymbol{\mu}, \mathbf{f}(t))$, is conserved along solutions of the system then and only then when the vector $\boldsymbol{\mu}$ is orthogonal to all the Boltzmann–Orlov–Moser–Bruno vectors [6–8]: $\boldsymbol{\alpha} - \boldsymbol{\beta}$. In this example, the Boltzmann–Orlov–Moser–Bruno vector is unique with accuracy to multiplier: $\boldsymbol{\alpha} - \boldsymbol{\beta} = (1, 1, -1, -1)$.

Thus, the stoichiometric number is the number of molecules participating in the reaction, S_i, $i = 1, 2, \ldots, n$, in (1.2) are the chemical symbols of the reacting molecules. Let us note that if the number of molecules in an elementary reaction of the form (1.2) is stored, then $|\boldsymbol{\alpha}| = |\boldsymbol{\beta}|$, where $|\boldsymbol{\alpha}| \equiv \alpha_1 + \alpha_2 + \cdots + \alpha_n$.

Namely the linear conservation laws are important when we study the H-theorem, they determine a stationary solution –the Boltzmann extremal –argument of conditional minimum of the H-function under condition that the constant of the linear conservation laws are fixed (by initial data).

The H-theorem is just the proof of the inequality: $dH(\mathbf{f})/dt \leq 0$, the proof of decreasing of some functional H along solutions of system of equations. The H-function for the chemical kinetics equations has the form:

$$H(\mathbf{f}) = \sum_{i=1}^{n} f_i \left(\ln \frac{f_i}{\xi_i} - 1\right). \tag{1.3}$$

Here the vector $\boldsymbol{\xi} = (\xi_1, \xi_2, \ldots, \xi_n)$, where $\xi_i > 0$, is a positive stationary solution of the system of the chemical kinetics equations. The H-function (1.3) with the minus sign is called the Kullback–Leibler information entropy [9].

In [4,5] the classification of the conditions on the coefficients of the physico-chemical kinetics equations (1.1) is presented, when the H-theorem is fulfilled. It is valid in the case of the symmetric constants of the reactions: $K^{\boldsymbol{\alpha}}_{\boldsymbol{\beta}} = K^{\boldsymbol{\beta}}_{\boldsymbol{\alpha}}$. A wider class of equations is when the condition of detailed balance is fulfilled, it is the following condition on the coefficients of system (1.1): let there exists at least one positive solution $\boldsymbol{\xi}$ of the following system of equations:

$$K^{\boldsymbol{\alpha}}_{\boldsymbol{\beta}} \boldsymbol{\xi}^{\boldsymbol{\alpha}} = K^{\boldsymbol{\beta}}_{\boldsymbol{\alpha}} \boldsymbol{\xi}^{\boldsymbol{\beta}}, \quad (\boldsymbol{\alpha}, \boldsymbol{\beta}) \in \Im. \tag{1.4}$$

Here the rate of the forward reaction equals the speed of reverse reaction for each of the reactions. The number of equations in the condition of detailed balance (1.4) equals to the number of reactions and the number of unknowns ξ_i is equal to n. And the most common condition, when the H-theorem is fulfilled, is the condition of dynamic equilibrium or the Stuckelberg–Batishcheva–Pirogov condition [4,5,10–12], when there exists at least one positive solution $\boldsymbol{\xi}$ of the following system of equations:

$$\sum_{\boldsymbol{\beta}} K^{\boldsymbol{\alpha}}_{\boldsymbol{\beta}}\boldsymbol{\xi}^{\boldsymbol{\alpha}} = \sum_{\boldsymbol{\beta}} K^{\boldsymbol{\beta}}_{\boldsymbol{\alpha}}\boldsymbol{\xi}^{\boldsymbol{\beta}}. \tag{1.5}$$

Here the sum of the rates of all reactions with the initial state $\boldsymbol{\alpha}$ is equal to the sum of all rates of the reactions with the final state $\boldsymbol{\alpha}$. The number of equations in the condition of dynamic equilibrium is equal to the number of different vectors $\boldsymbol{\alpha}$ (or different $\boldsymbol{\beta}$) in pairs $(\boldsymbol{\alpha}, \boldsymbol{\beta}) \in \Im$. Moreover, for each pair of states $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$ such that they transform only each other there is the pair of the same equations: $K^{\boldsymbol{\alpha}}_{\boldsymbol{\beta}}\boldsymbol{\xi}^{\boldsymbol{\alpha}} = K^{\boldsymbol{\beta}}_{\boldsymbol{\alpha}}\boldsymbol{\xi}^{\boldsymbol{\beta}}$, in the system of Eqs. (1.5). And the number of unknowns ξ_i in (1.5) is equal to n.

In 1952 year Stuckelberg (E.C.G. Stuckelberg) suggested the condition of dynamic equilibrium for the Boltzmann kinetic equation [12, formula (2.9) in p. 21]:

$$\int w\left(\Gamma', \Gamma'_1; \Gamma, \Gamma_1\right) d\Gamma' d\Gamma'_1 = \int w\left(\Gamma, \Gamma_1; \Gamma', \Gamma'_1\right) d\Gamma' d\Gamma'_1, \tag{1.6}$$

where the symbol Γ denotes the set of all variables on which the distribution function depends, with the exception of the coordinates of the molecule as a whole and time t, $w\left(\Gamma', \Gamma'_1; \Gamma, \Gamma_1\right)$ is a function of all its arguments defined by the collision with the transition $\Gamma, \Gamma_1 \to \Gamma', \Gamma'_1$, such that the ratio of $w\left(\Gamma', \Gamma'_1; \Gamma, \Gamma_1\right) d\Gamma' d\Gamma'_1$ to the absolute value of the relative speed of the colliding molecules has the dimension of area and represents the effective cross section of collisions. The possibility of transforming the collision integral for the Boltzmann equation with (1.6) was suggested by Stuckelberg. And for physico-chemical kinetics the condition of dynamic equilibrium is formulated and investigated in [4,5,10,11]. It is also called the Stuckelberg–Batishcheva–Pirogov condition.

Let the set $\Im$ contains only vectors having one component equal to one and the rest equal to zero: $|\boldsymbol{\alpha}| = |\boldsymbol{\beta}| = 1$ for all $(\boldsymbol{\alpha}, \boldsymbol{\beta}) \in \Im$. Then the system (1.1) is linear. Linear system (1.1) is the system of equations of a Markov process:

$$\frac{df_i}{dt} = \sum_{j=1}^{n}\left(K^{\mathbf{e}_j}_{\mathbf{e}_i} f_j - K^{\mathbf{e}_i}_{\mathbf{e}_j} f_i\right), \quad i = 1, 2, \ldots, n, \tag{1.7}$$

where $K^{\mathbf{e}_j}_{\mathbf{e}_i} > 0$ when $j \neq i$, $K^{\mathbf{e}_i}_{\mathbf{e}_i} = 0$. If the system is quadratic ($|\boldsymbol{\alpha}| = |\boldsymbol{\beta}| = 2$ for all $(\boldsymbol{\alpha}, \boldsymbol{\beta}) \in \Im$), in the symmetric case ($K^{\boldsymbol{\alpha}}_{\boldsymbol{\beta}} = K^{\boldsymbol{\beta}}_{\boldsymbol{\alpha}}$) we will obtain spatially homogeneous discrete velocity models of the Boltzmann equation. The system of coagulation–fragmentation equations will be obtained, if the set $\Im$ consists of pairs $(\boldsymbol{\alpha}, \boldsymbol{\beta})$ and $(\boldsymbol{\beta}, \boldsymbol{\alpha})$ such that $|\boldsymbol{\alpha}| = 2$ and $|\boldsymbol{\beta}| = 1$, and if the ith and jth components of the vector $\boldsymbol{\alpha}$ equal to one then the $(i + j)$th component of $\boldsymbol{\beta}$ will be equal to one.

Let us write the Markov process (1.7) in the form:

$$\frac{df_i}{dt} = \sum_{j=1}^{n} A^j_i f_j, \quad i = 1, 2, \ldots, n \tag{1.8}$$

where

$$A^j_i = K^{\mathbf{e}_j}_{\mathbf{e}_i} > 0 \quad \text{if } j \neq i, A^i_i = -\sum_j K^{\mathbf{e}_i}_{\mathbf{e}_j} \tag{1.9}$$

This form of the matrix A (1.9) automatically conserves positivity of $f_i\,(t)$ and ensures the conservation law of the total number of particles: $\frac{d}{dt}\sum_{i=1}^{n} f_i = 0$. The positivity conservation means that the positive cone: $\{\mathbf{f} \in R^n : \forall i = 1, 2, \ldots, n\, f_i > 0\}$, is mapping into itself, and if some but not all $f_i\,(0)$ is equal to zero, then $f_i\,(t)$ will be positive for $t > 0$. The reverse statement is also true –any linear system which has these two properties, gives for the matrix A condition of the off-diagonal positivity and equality to zero of the sum of elements of each column, i.e., the matrix A admits the representation (1.9) through some matrix $K^{\mathbf{e}_j}_{\mathbf{e}_i}$ of transition probabilities.

Let us turn to discrete time $t = 0, \tau, 2\tau, 3\tau, \ldots$, where $\tau > 0$, in the system (1.8), replacing the derivatives $\frac{df_i}{dt}$ by difference analogues $\frac{f_i(t+\tau)-f_i(t)}{\tau}$. If in the right side of (1.8) we take time t, i.e. we consider an explicit discretization in time, then we will get a Markov chain

$$f_i\,(t + \tau) = \sum_{j=1}^{n} B^j_i f_j\,(t)\,, \quad i = 1, 2, \ldots, n \tag{1.10}$$

where $B^j_i = \tau A^j_i$ when $j \neq i \quad B^i_i = 1 + \tau A^i_i$.

We note the following point, which we will need in the future. We have written the system of the chemical kinetics equations in the form of non-linear analogue of the Markov process (1.8):

$$\frac{df_i}{dt} = \sum_{j=1}^{n} A^j_i\,(\mathbf{f}\,(t))\, f_j, \quad i = 1, 2, \ldots, n, \tag{1.11}$$

where the matrix A now depends on $\mathbf{f}\left(t\right)$ (it is not yet imposed any restrictions). Then in the case of discretization in time of Eqs. (1.11) we get a nonlinear analogue of (1.10) which can be written in the form

$$f_i\left(t+\tau\right)=\sum_{j=1}^{n}B_i^j\left(\mathbf{f}\left(t\right)\right)f_j\left(t\right), \quad i=1,2,\ldots,n, \quad \text{where } B\left(\mathbf{f}\left(t\right)\right)=E+\tau A\left(\mathbf{f}\left(t\right)\right), \tag{1.12}$$

where E is the identity matrix of size $n\times n$.

The condition of conservation of positivity of $f_i\left(t\right)$ for (1.10) is the condition of positivity of all elements of the matrix B. It therefore gives the condition on τ:

$$0<\tau<1/\left(-A_i^i\right)=1/\sum_j K_{\mathbf{e}_j}^{\mathbf{e}_i}.$$

As the simplest example of a nonlinear system of equations of chemical kinetics we consider the Carleman model [13] (in the spatial homogeneous case) which is a system of two equations:

$$\begin{cases}\dfrac{df_1}{dt}=\sigma\left(f_2^2-f_1^2\right),\\[2mm] \dfrac{df_2}{dt}=\sigma\left(f_1^2-f_2^2\right).\end{cases} \tag{1.13}$$

It is a system of the physico-chemical kinetics equations with one reversible reaction $2S_1\to 2S_2$. (In this case constants of direct and reverse processes are equal –the symmetric case: $K_{(0,2)}^{(2,0)}=K_{(2,0)}^{(0,2)}=\sigma/2$.)

Let us turn to discrete time in (1.13):

$$\begin{cases}f_1\left(t+\tau\right)=f_1\left(t\right)+\tau\sigma\left(f_2^2\left(t\right)-f_1^2\left(t\right)\right),\\ f_2\left(t+\tau\right)=f_2\left(t\right)+\tau\sigma\left(f_1^2\left(t\right)-f_2^2\left(t\right)\right),\end{cases} \tag{1.14}$$

For the system (1.13) and its discretization (1.14) there is the only one (with accuracy to multiplication by a constant) linear conservation law which is the conservation law of number of particles: $f_1+f_2=A=const$. As $f_1^2-f_2^2=\left(f_1+f_2\right)\left(f_1-f_2\right)=A\left(f_1-f_2\right)$, then the system (1.13) reduces to the Markov process, (1.14) –to the Markov chain.

The system (1.14) will conserve positivity if and only if $0<\tau\sigma A<1$. So (1.14) will not conserve positivity for any $\tau>0$ (if we do not fix a constant of the linear conservation law A). But if the constant of the linear invariant is fixed, then there will be the condition of positivity: $0<\tau<1/(\sigma A)$. This feature we will take into account in further considerations.

2. The *H*-theorem for the explicit time discretization of the physico-chemical kinetics equations

In the case of explicit time discretization of the physico-chemical kinetics equations the H-theorem, generally speaking, is not valid. Let us consider an example showing this.

The system of the physico-chemical kinetics equations for the reaction $2S_1\to S_2$ in the case of symmetrical coefficients of reaction rates: $K_{(0,1)}^{(2,0)}=K_{(2,0)}^{(0,1)}=\sigma$, has the form:

$$\begin{cases}\dfrac{df_1}{dt}=2\sigma\left(f_2-f_1^2\right),\\[2mm] \dfrac{df_2}{dt}=\sigma\left(f_1^2-f_2\right).\end{cases}$$

Time discretization of this system gives the following system:

$$\begin{cases}f_1\left(t+\tau\right)=f_1\left(t\right)+2\tau\sigma\left(f_2\left(t\right)-f_1^2\left(t\right)\right),\\ f_2\left(t+\tau\right)=f_2\left(t\right)+\tau\sigma\left(f_1^2\left(t\right)-f_2\left(t\right)\right).\end{cases} \tag{2.1}$$

Let us show that the Kullback–Leibler entropy with minus sign (1.3):

$$H=\psi\left(f_1\right)+\psi\left(f_2\right), \tag{2.2}$$

where $\psi\left(x\right)=x\left(\ln x-1\right)$, can increase on the solutions of (2.1) such that

$$f_i\left(t\right)\geqslant 0 \quad \text{and} \quad f_i\left(t+\tau\right)>0 \quad \text{for } i=1,2.$$

$$H\left(t+\tau\right)=\psi\left(f_1\left(t+\tau\right)\right)+\psi\left(f_2\left(t+\tau\right)\right)=\psi\left(f_1\left(t\right)+2A\right)+\psi\left(f_2\left(t\right)-A\right), \tag{2.3}$$

where we introduce the notation

$$A\equiv\tau\sigma\left(f_2\left(t\right)-f_1^2\left(t\right)\right). \tag{2.4}$$

Let us fix the value of $f_2\left(t\right)$ by the value of $f_1\left(t\right)$ with the relation

$$f_2\left(t\right)=f_1\left(t\right)+A. \tag{2.5}$$

Then

$$A = \tau\sigma f_1(t)\,(1 - f_1(t))/(1 - \tau\sigma)\,. \tag{2.6}$$
$$H(t+\tau) - H(t) = \psi(f_1(t) + 2A) - \psi(f_1(t) + A)\,.$$

Let us take $f_1(t) + A$ equal to the value of argument in which the minimum of $\psi(x) = x(\ln x - 1)$ is achieved, i.e.

$$f_1(t) + A = 1. \tag{2.7}$$

Then we obtain that we have wanted to show: $H(t+\tau) > H(t)$, if

$$A \neq 0. \tag{2.8}$$

It remains only to check the conditions (2.3) and (2.8). From (2.6) to (2.8) we have

$$f_1(t) = \frac{1}{\tau\sigma} - 1, \quad A = 2 - \frac{1}{\tau\sigma}. \tag{2.9}$$

From (2.5) and (2.7) we obtain $f_2(t) = 1$. So from (2.1), (2.6), (2.9) we have

$$f_1(t+\tau) = 3 - \frac{1}{\tau\sigma}, \quad f_2(t+\tau) = \frac{1}{\tau\sigma} - 1.$$

Hence the condition (2.3) will be fulfilled, if we take $1/3 < \tau\sigma < 1$.

Let us consider the cases when the proof of the H-theorem for the physico-chemical kinetics equations with discrete time is reduced to its proof for Markov chains.

Let us take the reaction $S_1 + S_2 \to 2S_2$. The system of the chemical kinetic equation for it in the case of symmetrical constants of reactions: $K_{(0,2)}^{(1,1)} = K_{(1,1)}^{(0,2)} = \sigma$, has the form

$$\begin{cases} \dfrac{df_1}{dt} = \sigma\left(f_2^2 - f_1 f_2\right), \\ \dfrac{df_2}{dt} = \sigma\left(f_1 f_2 - f_2^2\right). \end{cases} \tag{2.10}$$

Time discretization of (2.10) gives

$$\begin{cases} f_1(t+\tau) = f_1(t) + \tau\sigma\left(f_2^2(t) - f_1(t) f_2(t)\right), \\ f_2(t+\tau) = f_2(t) + \tau\sigma\left(f_1(t) f_2(t) - f_2^2(t)\right), \end{cases} \tag{2.11}$$

(2.10) we may write in the form (1.11), where

$$A(\mathbf{f}(t)) = \begin{pmatrix} -f_2 & f_2 \\ f_2 & -f_2 \end{pmatrix}, \tag{2.12}$$

and (2.11) has the form (1.12). If the condition of conservation of positivity for (2.11): $f_2(0) > 0$, is fulfilled, then the expression (2.12) will determine doubly stochastic matrix $A(\mathbf{f}(t))$: $\sum_{i=1}^{n} A_i^j(\mathbf{f}(t)) = \sum_{j=1}^{n} A_i^j(\mathbf{f}(t)) = 0$, and in the case of discrete time: (2.11), we have doubly stochastic matrix $B(\mathbf{f}(t)) = E + \tau A(\mathbf{f}(t))$: $\sum_{i=1}^{n} B_i^j(\mathbf{f}(t)) = \sum_{j=1}^{n} B_i^j(\mathbf{f}(t)) = 1$, and the condition of conservation of positivity has the form: $f_2(0) > 0$, $\tau < 1/(\sigma N)$, where $N \equiv f_1 + f_2 = const$. Just because of the doubly stochasticity of $A(\mathbf{f}(t))$ and $B(\mathbf{f}(t))$ the H-theorem for systems (2.10), (2.11) is valid with the same H-function as for the Markov processes and chains in the case of doubly stochasticity: $H = \sum_{i=1}^{2} \psi(f_i)$, where $\psi(x)$ is an arbitrary strictly convex function. The same situation occurs for the Carleman model (1.13), (1.14),when $A(\mathbf{f}(t)) = \begin{pmatrix} -(f_1+f_2) & (f_1+f_2) \\ (f_1+f_2) & -(f_1+f_2) \end{pmatrix}$. Let us consider more general situation than reduction to the case of the doubly stochastic matrix.

Let we have written the system of the physico-chemical kinetics equations in the form of non-linear analogue of the Markov process (1.11). Then for time discretization of the system (1.11) we get a nonlinear analogue of the Markov chain (1.12).

Let us consider the H-function such as for Markov processes and chains:

$$H = \sum_{i=1}^{n} \xi_i \psi(f_i/\xi_i) \tag{2.13}$$

where $\psi(x)$ is an arbitrary strictly convex function. The following theorem is valid.

Theorem 2.1. *Let in (1.12) matrix $B(\mathbf{f}(t))$ is stochastic:*

$$B_i^j(\mathbf{f}(t)) > 0, \tag{2.14}$$

$$\sum_{i=1}^{n} B_i^j(\mathbf{f}(t)) = 1, \tag{2.15}$$

and let vector $\boldsymbol{\xi} = (\xi_1, \xi_2, \ldots, \xi_n)$ *with positive components exists such that*

$$\sum_{j=1}^{n} B_i^j\left(\mathbf{f}\left(t\right)\right)\xi_j = \xi_i. \tag{2.16}$$

Then the next statements are valid

(a)*The H-function (2.13) does not increase on the solutions of system (1.12):* $\Delta H \leq 0$*, moreover, equality is achieved only in stationary points (like for Markov chains). All stationary points have the form:*

$$\mathbf{f}_0 = \lambda\boldsymbol{\xi}. \tag{2.17}$$

(b) *The system (1.12) has the unique (up to a constant multiplier) conservation law of the form* $\sum_{i=1}^{n}\mu_i f_i$*, i.e. the only linear invariant on the solutions of the system (1.12), which is the conservation law of the number of all particles in the system* $\sum_{i=1}^{n} f_i\left(t\right)$*:*

$$\sum_{i=1}^{n} f_i\left(t\right) = A = const. \tag{2.18}$$

Stationary solution of system (1.12) with positive components will be unique, if the constant of the linear conservation law A is fixed. It is found as a conditional minimum of the H-function under the condition that the constant of the linear conservation law A is fixed, and is given by the formula

$$\mathbf{f}_0 = \left(A \Big/ \sum_{i=1}^{n}\xi_i\right)\boldsymbol{\xi}. \tag{2.19}$$

(c) *Such stationary solution will exist if A is determined by the initial condition* $\mathbf{f}\left(0\right)$ *with positive components:* $A = \sum_{i=1}^{n} f_i\left(0\right)$*. The solution* $\mathbf{f}\left(t\right)$ *with this initial condition exists for all* $t = 0, \tau, 2\tau, \ldots$*, is unique and tends to the stationary solution of (2.19).*

The proof.

(a) According to (1.12)

$$\begin{aligned} H\left(t+\tau\right) &= \sum_{i=1}^{n}\xi_i\psi\left(f_i\left(t+\tau\right)/\xi_i\right) = \sum_{i=1}^{n}\xi_i\psi\left(\sum_{j=1}^{n}\left(\frac{B_i^j\left(\mathbf{f}\left(t\right)\right)\xi_j}{\xi_i}\right)\frac{f_j\left(t\right)}{\xi_j}\right) \leq^{(1)} \sum_{i=1}^{n}\xi_i\sum_{j=1}^{n}\frac{B_i^j\left(\mathbf{f}\left(t\right)\right)\xi_j}{\xi_i}\psi\left(\frac{f_j\left(t\right)}{\xi_j}\right) \\ &= \sum_{i,j=1}^{n} B_i^j\left(\mathbf{f}\left(t\right)\right)\xi_j\psi\left(\frac{f_j\left(t\right)}{\xi_j}\right) = \sum_{j=1}^{n}\left(\sum_{i=1}^{n}B_i^j\left(\mathbf{f}\left(t\right)\right)\right)\xi_j\psi\left(\frac{f_j\left(t\right)}{\xi_j}\right) =^{(2)} \sum_{j=1}^{n}\xi_j\psi\left(\frac{f_j\left(t\right)}{\xi_j}\right) = H\left(t\right). \end{aligned} \tag{2.20}$$

Here in (1) we are able to apply the Jensen's inequality for convex function ψ, since $\sum_{j=1}^{n}B_i^j\left(\mathbf{f}\left(t\right)\right)\xi_j/\xi_i = 1$, and the equality in (1) is achieved if $f_i/\xi_i = f_j/\xi_j$ for all $i, j = 1, 2, \ldots, n$, i.e. only at stationary points, and any stationary point can be represented in the form (2.17). In (2) we have used the condition (2.15). So, the proof of the inequality in the H-theorem (2.20) is the same as for Markov chains.

(b) According to the condition (2.15) we rewrite the system (1.12) in the following form:

$$f_i\left(t+\tau\right) = f_i\left(t\right) + \sum_{j=1}^{n}B_i^j\left(\mathbf{f}\left(t\right)\right)f_j\left(t\right) - \sum_{j=1}^{n}B_j^i\left(\mathbf{f}\left(t\right)\right)f_i\left(t\right). \tag{2.21}$$

Then the condition of stationarity of the solution (2.16) has the form:

$$\sum_{j=1}^{n}B_i^j\left(\mathbf{f}\left(t\right)\right)\xi_j - \sum_{j=1}^{n}B_j^i\left(\mathbf{f}\left(t\right)\right)\xi_i = 0. \tag{2.22}$$

From (2.21) we obtain

$$\sum_{i=1}^{n}\mu_i f_i\left(t+\tau\right) = \sum_{i=1}^{n}\mu_i f_i\left(t\right) + \sum_{i,j=1}^{n}\mu_i B_i^j\left(\mathbf{f}\left(t\right)\right)f_j\left(t\right) - \sum_{i,j=1}^{n}\mu_i B_j^i\left(\mathbf{f}\left(t\right)\right)f_i\left(t\right).$$

Changing places i and j in the latest term we have:

$$\sum_{i=1}^{n}\mu_i f_i\left(t+\tau\right) = \sum_{i=1}^{n}\mu_i f_i\left(t\right) + \sum_{i,j=1}^{n}\left(\mu_i - \mu_j\right)B_i^j\left(\mathbf{f}\left(t\right)\right)f_j\left(t\right). \tag{2.23}$$

This shows that if all μ_i are the same, we get a linear conservation law. Let us prove the converse statement. We denote $y_i\left(t\right) \equiv f_i\left(t\right)/\xi_i$. From (2.23) we obtain:

$$\sum_{i=1}^{n}\mu_i f_i\left(t+\tau\right) = \sum_{i=1}^{n}\mu_i f_i\left(t\right) - \sum_{i,j=1}^{n}B_i^j\left(\mathbf{f}\left(t\right)\right)\xi_j y_i\left(t\right)\left(\mu_j - \mu_i\right)\frac{y_j\left(t\right)}{y_i\left(t\right)}. \tag{2.24}$$

Multiplying both parts of (2.22) on $y_i(t)$ and summing , we get

$$\sum_{i,j=1}^{n} B_i^j(\mathbf{f}(t))\,\xi_j y_i(t) - \sum_{i,j=1}^{n} B_j^i(\mathbf{f}(t))\,\xi_i y_i(t) = 0.$$

Changing places i and j in the second term we have

$$\sum_{i,j=1}^{n} B_i^j(\mathbf{f}(t))\,\xi_j y_i(t)\left(1 - \frac{y_j(t)}{y_i(t)}\right) = 0. \tag{2.25}$$

Subtracting from (2.24) the zero component (2.25) and taking $y_i = \exp(\mu_i)$ we obtain

$$\sum_{i=1}^{n} \mu_i f_i(t+\tau) = \sum_{i=1}^{n} \mu_i f_i(t) - \sum_{i,j=1}^{n} B_i^j(\mathbf{f}(t))\,\xi_j y_i(t)\left[\left(\mu_j - \mu_i\right)\exp\left(\mu_j - \mu_i\right) - \exp\left(\mu_j - \mu_i\right) + 1\right].$$

Due to the inequality $u \exp u - \exp u + 1 \geq 0$, where equality is achieved only when $u = 0$, we perceive that $\sum_{i=1}^{n} \mu_i f_i \equiv (\boldsymbol{\mu}, \mathbf{f})$ is a linear conservation law only if all the components of the vector $\boldsymbol{\mu}$ are equal to each other.

The unique stationary point is founded by the substitution (2.17) into (2.18), and we get the expression (2.19). The result of varying the H-function under condition of the conservation law of number of particles gives the same answer –the expression (2.19).

(c) Such stationary point with positive coordinates exists due to $A > 0$, since A is defined through positive initial data. Due to the conditions (2.14) the system (1.12) conserves positivity, so its solution exists for all times in a positive cone $\{\mathbf{f} \in \mathbb{R}^n : \forall i = 1, 2, \ldots, n\, f_i > 0\}$. The intersection of the positive cone and the conservation law of the number of all particles gives a bounded set. Therefore, all solutions such that holds (2.18) converge to a stationary point (2.19) because of the strictness of the inequality in other points of the closure of this set.

Theorem 2.1 has been proved.

For the case of continuous time, i.e. for the system (1.11) we have a similar result, since the proof of the inequality of the H-theorem (with the H-function (2.13)) is the same as for Markov processes.

So, the H-theorem is also valid for nonsymmetric generalizations (1.13) and (1.14):

$$\begin{cases} \dfrac{df_1}{dt} = K_{(1,1)}^{(0,2)} f_2^2 - K_{(0,2)}^{(1,1)} f_1 f_2, \\ \dfrac{df_2}{dt} = K_{(0,2)}^{(1,1)} f_1 f_2 - K_{(1,1)}^{(0,2)} f_2^2, \end{cases}$$

$$\begin{cases} f_1(t+\tau) = f_1(t) + \tau\left(K_{(1,1)}^{(0,2)} f_2^2 - K_{(0,2)}^{(1,1)} f_1 f_2\right), \\ f_2(t+\tau) = f_2(t) + \tau\left(K_{(0,2)}^{(1,1)} f_1 f_2 - K_{(1,1)}^{(0,2)} f_2^2\right). \end{cases}$$

This requires the fulfillment the condition of the positivity conservation. For the latest system

$$B(\mathbf{f}(t)) = \begin{pmatrix} 1 - \tau K_{(0,2)}^{(1,1)} f_2 & \tau K_{(1,1)}^{(0,2)} f_2 \\ \tau K_{(0,2)}^{(1,1)} f_2 & 1 - \tau K_{(1,1)}^{(0,2)} f \end{pmatrix},$$

and the condition of the positivity conservation has the form: $f_2(0) > 0$, $\tau < 1/\left(\max(K_{(0,2)}^{(1,1)}, K_{(1,1)}^{(0,2)})N\right)$, where $N \equiv f_1 + f_2 = const$. A positive components of vector $\boldsymbol{\xi} = (\xi_1, \xi_2)$ for the H-function (2.13) (where $n = 2$) is determined from the equality $K_{(1,1)}^{(0,2)} \xi_2 - K_{(0,2)}^{(1,1)} \xi_1$.

Under the condition of the Theorem 2.1 is not only the Carleman model with discrete time, but the system of equations of chemical kinetics for any reaction of the form $mS_1 \to mS_2$, where m is any natural number, with any constants for the forward reaction ($K_{(0,m)}^{(m,0)}$) and reverse one ($K_{(m,0)}^{(0,m)}$):

$$\begin{cases} f_1(t+\tau) = f_1(t) + \tau\left(K_{(m,0)}^{(0,m)} f_2^m - K_{(0,m)}^{(m,0)} f_1^m\right), \\ f_2(t+\tau) = f_2(t) + \tau\left(K_{(0,m)}^{(m,0)} f_1^m - K_{(m,0)}^{(0,m)} f_2^m\right). \end{cases}$$

You need to take the matrix $B(\mathbf{f}(t))$ the following:

$$\begin{pmatrix} 1 - \tau \sqrt[m]{K_{(0,m)}^{(m,0)}}\, c(\mathbf{f}(t)) & \tau \sqrt[m]{K_{(m,0)}^{(0,m)}}\, c(\mathbf{f}(t)) \\ \tau \sqrt[m]{K_{(0,m)}^{(m,0)}}\, c(\mathbf{f}(t)) & 1 - \tau \sqrt[m]{K_{(m,0)}^{(0,m)}}\, c(\mathbf{f}(t)) \end{pmatrix},$$

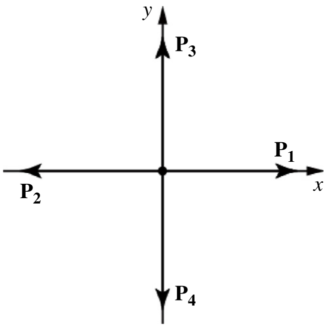

Fig. 1. The Broadwell model.

where $c(\mathbf{f}(t)) = \sum_{i=0}^{m-1}\left(\sqrt[m]{K_{(0,m)}^{(m,0)}}f_1\right)^{m-1-i}\left(\sqrt[m]{K_{(m,0)}^{(0,m)}}f_2\right)^{i}$. The condition of the positivity conservation is

$$\tau < \left[\max\left(\sqrt[m]{K_{(0,m)}^{(m,0)}}, \sqrt[m]{K_{(m,0)}^{(0,m)}}\right) \times \sum_{i=0}^{m-1}\left(\sqrt[m]{K_{(0,m)}^{(m,0)}}\right)^{m-1-i}\left(\sqrt[m]{K_{(m,0)}^{(0,m)}}\right)^{i}\max\left(N^{m-1}, 1\right)\right]^{-1},$$

where $N \equiv f_1 + f_2 = const$. A positive components of vector $\boldsymbol{\xi} = (\xi_1, \xi_2)$ for the H-function (2.13) (where $n = 2$) is determined from equality $K_{(m,0)}^{(0,m)}\xi_2^m = K_{(0,m)}^{(m,0)}\xi_1^m$.

In the next section we consider the time discretization for one of the simplest discrete models of the Boltzmann equation –for the Broadwell model [14].

3. The H-theorem for the Broadwell model with discrete time

The Broadwell model [4,14,15] represents the following system of one-component gas with a mass of molecule m. The first kind of particles with momentum $\mathbf{p}_1$ collides with a second kind of particles having a momentum $\mathbf{p}_2$, and they give the third and fourth sorts of particles with momenta $\mathbf{p}_3$ and $\mathbf{p}_4$ respectively, and vice versa: particles of the third and fourth kinds after the collision give the particles of the first and second sort (see Fig. 1). Here $|\mathbf{p}_i| = p$ for $i = 1, 2, 3, 4$. The conservation laws of momentum: $\mathbf{p}_1 + \mathbf{p}_2 = \mathbf{p}_3 + \mathbf{p}_4$, and energy: $\frac{\mathbf{p}_1^2}{2m} + \frac{\mathbf{p}_2^2}{2m} = \frac{\mathbf{p}_3^2}{2m} + \frac{\mathbf{p}_4^2}{2m}$, are valid.

We have the next system of equations:

$$\begin{cases} \dfrac{\partial f_1}{dt} + \dfrac{p}{m}\dfrac{\partial f_1}{\partial x} = \sigma\left(f_3f_4 - f_1f_2\right), \\ \dfrac{\partial f_2}{dt} + \dfrac{p}{m}\dfrac{\partial f_2}{\partial x} = \sigma\left(f_3f_4 - f_1f_2\right), \\ \dfrac{\partial f_3}{dt} + \dfrac{p}{m}\dfrac{\partial f_3}{\partial y} = \sigma\left(f_1f_2 - f_3f_4\right), \\ \dfrac{\partial f_4}{dt} + \dfrac{p}{m}\dfrac{\partial f_4}{\partial y} = \sigma\left(f_1f_2 - f_3f_4\right). \end{cases}$$

Spatially homogeneous version of the Broadwell model is a system of equations of physico-chemical kinetics with one reversible reaction $S_1 + S_2 \to S_3 + S_4$ with the symmetric constants of the forward and reverse reactions any of which is equal to σ: $K_{(0,0,1,1)}^{(1,1,0,0)} = K_{(1,1,0,0)}^{(0,0,1,1)} = \sigma$. Here S_i corresponds to the ith sort of particles (with momentum $\mathbf{p}_i$).

Let us consider the spatially homogeneous version of the Broadwell model with discrete time:

$$\begin{cases} f_1(t+\tau) = f_1 + \tau\sigma\left(f_3f_4 - f_1f_2\right), \\ f_2(t+\tau) = f_2 + \tau\sigma\left(f_3f_4 - f_1f_2\right), \\ f_3(t+\tau) = f_3 + \tau\sigma\left(f_1f_2 - f_3f_4\right), \\ f_4(t+\tau) = f_4 + \tau\sigma\left(f_1f_2 - f_3f_4\right). \end{cases} \tag{3.1}$$

Here and further in the right parts $f_i \equiv f_i(t)$.

There are three linear conservation laws for (3.1): the conservation law of number of particles, which coincides with the conservation law of energy:

$$f_1 + f_2 + f_3 + f_4 = N, \tag{3.2}$$

and the conservation laws of the momentum components:

$$\begin{cases} f_1 - f_2 = P_x, \\ f_3 - f_4 = P_y. \end{cases} \tag{3.3}$$

(3.2) and (3.3) can be rewritten in the following four types of expressing all f_i through f_1 or through f_2 or through f_3 or through f_4:

$$\begin{cases} \qquad f_2 = f_1 - P_x, \\ f_3 = \left(N + P_x + P_y\right)/2 - f_1, \\ f_4 = \left(N + P_x - P_y\right)/2 - f_1, \end{cases} \tag{3.4}$$

$$\begin{cases} \qquad f_1 = f_2 + P_x, \\ f_3 = \left(N - P_x + P_y\right)/2 - f_2, \\ f_4 = \left(N - P_x - P_y\right)/2 - f_2, \end{cases} \tag{3.5}$$

$$\begin{cases} f_1 = \left(N + P_x + P_y\right)/2 - f_3, \\ f_2 = \left(N - P_x + P_y\right)/2 - f_3, \\ \qquad f_4 = f_3 - P_y, \end{cases} \tag{3.6}$$

$$\begin{cases} f_1 = \left(N + P_x - P_y\right)/2 - f_4, \\ f_2 = \left(N - P_x - P_y\right)/2 - f_4, \\ \qquad f_3 = f_4 + P_y. \end{cases} \tag{3.7}$$

Due to (3.1), (3.4), (3.6)

$$\begin{aligned} f_1\left(t+\tau\right) &= f_1 + \tau\sigma\left(f_3\left(\left(N+P_x-P_y\right)/2 - f_1\right) - f_1\left(\left(N-P_x+P_y\right)/2 - f_3\right)\right) \\ &= f_1 + \tau\sigma\left(f_3\left(N+P_x-P_y\right)/2 - f_1\left(N-P_x+P_y\right)/2\right), \end{aligned} \tag{3.8}$$

$$\begin{aligned} f_3\left(t+\tau\right) &= f_3 + \tau\sigma\left(f_1\left(\left(N-P_x+P_y\right)/2 - f_3\right) - f_3\left(\left(N+P_x-P_y\right)/2 - f_1\right)\right) \\ &= f_3 + \tau\sigma\left(f_1\left(N-P_x+P_y\right)/2 - f_3\left(N+P_x-P_y\right)/2\right). \end{aligned} \tag{3.9}$$

Because of (3.1), (3.5), (3.7)

$$\begin{aligned} f_2\left(t+\tau\right) &= f_2 + \tau\sigma\left(\left(\left(N-P_x+P_y\right)/2 - f_2\right)f_4 - \left(\left(N+P_x-P_y\right)/2 - f_4\right)f_2\right) \\ &= f_2 + \tau\sigma\left(f_4\left(N-P_x+P_y\right)/2 - f_2\left(N+P_x-P_y\right)/2\right), \end{aligned} \tag{3.10}$$

$$\begin{aligned} f_4\left(t+\tau\right) &= f_4 + \tau\sigma\left(\left(\left(N+P_x-P_y\right)/2 - f_4\right)f_2 - \left(\left(N-P_x+P_y\right)/2 - f_2\right)f_4\right) \\ &= f_4 + \tau\sigma\left(f_2\left(N+P_x-P_y\right)/2 - f_4\left(N-P_x+P_y\right)/2\right). \end{aligned} \tag{3.11}$$

Due to (3.8)–(3.11) instead of (3.1) we obtain Markov chain with matrix

$$\begin{pmatrix} 1-a & 0 & b & 0 \\ 0 & 1-b & 0 & a \\ a & 0 & 1-b & 0 \\ 0 & b & 0 & 1-a \end{pmatrix}, \tag{3.12}$$

where

$$\begin{aligned} a &\equiv \tau\sigma\left(N - P_x + P_y\right)/2 = f_2 + f_3, \\ b &\equiv \tau\sigma\left(N + P_x - P_y\right)/2 = f_1 + f_4. \end{aligned} \tag{3.13}$$

The condition of positivity for the Markov chain with the matrix (3.12), (3.13) has the form: $0 < a < 1$, $0 < b < 1$, and gives restrictions on the time step τ.

For Markov chains with matrix $n \times n$ with positive stationary solution $\xi = (\xi_1, \xi_2, \ldots, \xi_n)$ the H-theorem with the H-function (2.13) is valid. As for (3.12) we can take, for example, $\xi = (b, a, a, b)$. So, the H-theorem gives a stable stationary solutions such that $f_1/b = f_3/a$ and $f_2/a = f_4/b$, i.e.

$$f_1/f_3 = f_4/f_2 = b/a. \tag{3.14}$$

The Markov chain with the matrix (3.12), (3.13) has two conservation laws: (3.13), the Broadwell model (3.1) has three ones: (3.2), (3.3), and both systems give the same stationary solution.

The system (3.13) is equivalent to the following one:

$$\begin{aligned} f_1 + f_2 + f_3 + f_4 &= N, \\ f_1 - f_2 - f_3 + f_4 &= P_x - P_y. \end{aligned} \tag{3.15}$$

Due to (3.15) the H-function for the Broadwell model must be obtained from (2.13) according to one of the conservation laws (3.3). But the question remains –how?

We only note the following. Let $\psi(x) = x(\ln x - 1)$ in (2.13), then (2.13) will be rewritten in the form (1.3):

$$H = \sum_{i=1}^{4} f_i\left(\ln\frac{f_i}{\xi_i} - 1\right) = \sum_{i=1}^{4} f_i \ln f_i - \sum_{i=1}^{4} f_i \ln \xi_i - \sum_{i=1}^{4} f_i = \sum_{i=1}^{4} f_i \ln f_i - (b\ln b + a\ln a) - (b + a)\,.$$

In the latest equality we have taken $\xi = (b, a, a, b)$ and have used (3.13). Thus, if we take $\psi(x) = x(\ln x - 1)$ the H-function (2.13) coincides with the unique H-function for the Broadwell model [16].

4. Conclusion

The present paper is devoted to consideration of the H-theorem for equations of physico-chemical kinetics with an explicit discretization in time. As we saw in Section 1, the H-theorem for them, generally speaking, is not valid, but there are cases when its proof for the physico-chemical kinetics equations is reduced to the proof for Markov chains. Therefore it is interesting to considerate the H-theorem for implicit discretization in time for the physico-chemical kinetics equations and their generalizations, including the quantum physico-chemical kinetics [17].

There is a new form of the H-theorem in the papers of H. Poincare [18], V.V. Kozlov [19] and D. Treshchev [20]. It is valid for the Liouville equation and its generalizations [17–21]. There the concept of the Boltzmann extremal is also work [17,21]: it coincides with a time mean (the Cesaro mean), and this makes it a generally mathematical and fundamental as a method of search of stationary solutions of general class of equations as a linear such as Liouville equation, and nonlinear ones, and as a broad generalization of the concept of the entropy.

The present paper was not required the Cesaro means because a limit exists when time tends to infinity. The reason for the existence of the limit that we have considered the condition of positivity conservation (the elements of the matrix B have been positive). If instead of it we consider the condition of the nonnegativity conservation of the function that is the solution then the elements of the matrix B will be non-negative, and in the case of discrete time even for Markov chains the convergence is not always valid, but the Cesaro means coincide with the Boltzmann extremals.

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