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THERMODYNAMIC APPROACH TO QUALITATIVE PROPERTIES OF TRAJECTORIES OF HEAT AND MASS TRANSFER IN GAS–SOLID FLOW SYSTEMS—II. REACTING SYSTEMS

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Abstract—This article represents the second part of the work originated in [1]. Study is made of qualitative properties and stability of trajectories of simultaneous heat and mass transfer in reacting flow systems. For systems where the singular point is of quasi-equilibrium type the thermodynamic Liapunov function, V, resulting from the entropy balance, is an efficient stability (or instability) criterion. Whereas in the case of stationary non-equilibrium singular point a generalized function V_s, defined as the sum of V and some "kinetic" term, is suitable for predicting the qualitative properties and stability of trajectories.

NOMENCLATURE

$\mathbf{A}$,	$= [a_{ik}]$, matric of coefficients a_{ik}, equation (32);
A,B,C,D,	components of reacting fluid;
a,	ratio of heat exchange area and volume of catalytic zone $[\mathrm{m}^{-1}]$;
B,	$= kF/v_r$, volumetric coefficient of heat exchange (in computations B was taken as 23168.6) $[\mathrm{kJ\ K^{-1}\ h^{-1}\ m^{-3}}]$;
$\mathbf{B}$,	$= [b_{ik}]$, matrix of second order derivatives in Taylor expansion of function V;
c_A, c_B, c_D,	invariants, relating concentrations of components A, B, D and C $[\mathrm{kg\ kg^{-1}}]$;
c_p,	specific heat at constant pressure $[\mathrm{kJ\ kmol^{-1}\ K^{-1}}]$;
$\mathbf{D}$,	symmetric matrix of function V_s defined in terms of matrices $\mathbf{A}$ and $\mathbf{B}$;
E_1, f_1,	activation energy and frequency factor, respectively, equation (24) $[\mathrm{kJ\ kmol^{-1}}]$;
h,	apparatus length $[\mathrm{kJ\ kmol^{-1}}]$;
$\Delta\bar{H}$,	molar heat of reaction $[\mathrm{kJ\ kmol^{-1}}]$;
i,	specific enthalpy of solution $[\mathrm{kJ\ kg^{-1}}]$;
$\mathbf{K}$,	$\equiv \mathbf{A}^{-1\mathrm{T}}(\mathbf{D}-\mathbf{B})\mathbf{A}^{-1}$, "kinetic matrix";
k,	heat exchange coefficient $[\mathrm{kJ\ m^{-2}K^{-1}h^{-1}}]$;
M_C,	molar mass of component C $[\mathrm{kg\ kmol^{-1}}]$;
S,	specific entropy of solution $[\mathrm{kJ\ K^{-1}kg^{-1}}]$;
T,	temperature [K];
t,	space time [schemes (a) and (b), Fig. 1] or chronological time [scheme (c), Fig. 1];
$V, \tilde{V}$,	thermodynamic Liapunov functions $[\mathrm{kJ\ kg^{-1}}]$ or $[\mathrm{kJkg^{-1}K^{-1}}]$;
v_r,	reactor volume $[\mathrm{m^3}]$;
V_s,	"non-classical" thermodynamic Liapunov function $[\mathrm{kJ\ kg^{-1}}]$;
W,	reactants flow $[\mathrm{kg\ h^{-1}}]$;
$\mathbf{w}$,	w_A, w_B, w_C, w_D, mass fractions of reactants A, B, C and D in reacting solution $[\mathrm{kg\ kg^{-1}}]$;
$\mathbf{x}$,	state vector.

Greek symbols

θ,	average residence time in reactor [h];
$\Delta\bar{\mu}$,	chemical affinity $[\mathrm{kJ\ kmol^{-1}}]$;
μ_A, μ_B, μ_C,	partial thermodynamic potentials of reactants $[\mathrm{kJ\ kmol^{-1}}]$;
ε,	catalyst porosity;
ρ,	density of reacting solution $[\mathrm{kg\ m^{-3}}]$;
σ,	entropy source $[\mathrm{kJ\ K^{-1}m^{-3}h^{-1}}]$;
ν,	stoichiometic coefficient.

Subscripts

f,	final state;
h,	unreacting fluid exchanging heat;
i,	initial state;
M,	two-phase quantity related to the unit mass flow in reaction zone.

1. INTRODUCTION

IN [1] THE thermodynamic approach was used to investigate the qualitative properties of the trajectories of stationary coupled heat and mass transfer processes occurring in chemically inactive flow systems. We have analysed those non-reacting systems which were characterized by the quasi-equilibrium singular point‡ of the related ordinary differential equations. The analysis in [1] has included the reduction of coordinates for the differential equations of the system, by separating so called process invariants (i.e. the quantities that do not

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‡The process at a singular point is equilibrium, quasi-equilibrium or steady. In the state of quasi-equilibrium (typical of concurrent and counter-current flow processes) some small quantity of heat dissipation, because of phase slip, takes place. It is negligible.

change during process course), determination of the coordinates of the singular point corresponding with the defined values of invariants as well as the construction of the Liapunov's function constituting the stability criterion of the singular state and also the criterion of the qualitative properties of trajectories. The Liapunov functions have been constructed in [1] on the basis of the entropy balance as some "thermodynamic potentials of the flow processes", V, which constitute the appropriate counterparts of the usual thermodynamic potentials of closed systems.

The present article contains both an extension of the theory [1] to the processes with chemical reaction as well as dealing with the situation when the thermodynamic approach ceases to be efficient. The article is composed of two parts. In the first one the process of the chemical synthesis that occurs in the stationary concurrent and countercurrent systems is examined, Fig. 1, schemes (a) and (b). For such systems, which are characterized by a quasi-equilibrium singular point, the effectiveness of the purely thermodynamical Liapunov function V is proved. In the second part the unsteady state process in continuous flow stirred-tank reactor (CSTR) [Fig. 1, scheme (c)] is investigated. This reactor constitutes the more complicated system due to the non-equilibrium singular state. It will be shown that, in consideration of this non-equilibrium state, the purely thermodynamic criterion V may fail when determining the stability and, therefore, some generalized function, V_s, will be proposed. This function does not have a purely thermodynamic origin as, apart from the thermodynamic terms, it includes the terms connected with the kinetics of reactions.

The advantage of the function V_s is that in a sufficiently small finite surrounding of the singular point its time derivative $\dot{V}_s$ is always of definite sign (this cannot always be said about V in the case of non-equilibrium). Thanks to this property V_s makes it possible to prove the stability or instability of the singular point (according to Liapunov's second theorem or Chetayev's theorem, respectively [2]) as well as the stability (or instability) of trajectories in some finite region where the derivative $\dot{V}_s$ has a constant sign.

It must be stressed that, given a problem, the same mathematical method (the second Liapunov method) may be used to two different purposes.

In the case of the stationary flow processes [Fig. 1, schemes (a) and (b)] developing in the space along the apparatus axis, attention is paid to the qualitative properties of the family of trajectories found in the neighbourhood of the singular point. Each member of this family refers to the stationary process. In this case the purpose of the analysis is usually to perform a qualitative survey as well as to select a trajectory which can be considered the best of all steady trajectories.

However, in the case of the unsteady processes [Fig. 1, scheme (c)] developing in chronological time, Liapunov's second method is most often used in order to determine the stability (or instability) of the dynamical system which is subject to perturbations.

2. MATHEMATICAL MODEL OF THE PROCESSES WITH THE QUASI-EQUILIBRIUM SINGULAR STATE

In order to show the effectiveness of the purely thermodynamic approach for the quasi-equilibrium state we shall consider the changes in temperature and concentration of the auto-thermal concurrent and countercurrent tubular reactors [Fig. 1, schemes (a) and (b)]. Reactors of this type have important applications, for example in the process of ammonia synthesis.

During the exothermic reaction,

$$\nu_A A + \nu_B B = \nu_C C, \qquad (1)$$

heat exchange occurs between the reactive catalytic zone and the non-reactive non-catalytic zone, in which the reactants are heated. It is assumed that besides the reactants A, B, C, there is the non-reacting component, D, in the fluid. Changes of the process state in the space time, t, may be characterized by the two differential equations [(2) and (3)] describing respectively, the mass balance of the component C as well as the heat balance:

$$\frac{\mathrm{d}w_C}{\mathrm{d}t} = r_C \cdot M_C(\varepsilon \cdot \rho)^{-1} \qquad (2)$$

$$\frac{\mathrm{d}T}{\mathrm{d}t} = \{-\Delta\bar{H}r_C + ka(T_\mathrm{h} - T)\}\,(\rho\varepsilon c_\mathrm{p})^{-1} \qquad (3)$$

[see also equation (24)].

The remaining variables characterizing the system may be computed from invariants resulting correspondingly from the conservation of the number of atoms of elements:

$$c_A = w_A + w_C\frac{\nu_A M_A}{\nu_C M_C} = w_{\mathrm{i}A} + w_{\mathrm{i}C}\frac{\nu_A M_A}{\nu_C M_C}, \qquad (4)$$

$$c_B = w_B + w_C\frac{\nu_A M_A}{\nu_C M_C} = w_{\mathrm{i}B} + w_{\mathrm{i}C}\frac{\nu_A M_A}{\nu_C M_C}, \qquad (5)$$

$$c_D = w_D = w_{\mathrm{i}D}, \qquad (6)$$

as well as from the conservation of energy:

$$i(T, \mathbf{w}) - i_\mathrm{h}(T_\mathrm{h}, \mathbf{w}_\mathrm{i}) = i_\mathrm{M} = 0 \qquad \text{(countercurrent reactor)} \quad (7)$$

$$i_\mathrm{h}(T_\mathrm{h}, \mathbf{w}_\mathrm{i}) + i(T, \mathbf{w}) = i_\mathrm{M} = \text{const}^* \qquad \text{(concurrent reactor).} \quad (8)$$

Note that if the reactors were not auto-thermal then the quotient of the mass flow rates of phases flowing through each zone would appear in equations (7) and (8).

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*The value of invariant i_M can be computed from the knowledge of enthalpies i_h and i in a definite section of the reactor. Then solution of equation (8) together with $\dot{w}_C = 0$ and $\dot{T} = 0$ [equations (2) and (3)] makes it possible to determine the parameters of the singular point T_i^0 and w_C^0 [see also equations (9) and (10)].

Since we are dealing with flow processes it appears from equations (2) and (3) that the singular point is the state of thermodynamic quasi-equilibrium for which the following conditions must be satisfied:

$$T_h^0 = T^0, \tag{9}$$

$$\Delta\bar{\mu} = 0, \tag{10}$$

where

$$\Delta\bar{\mu} = \nu_C^{-1}(\nu_C M_C \mu_C - \nu_A M_A \mu_A - \nu_B M_B \mu_B)$$

[of course (10) is equivalent to the condition $r_C = 0$].

3. CONSTRUCTION OF THE THERMODYNAMIC LIAPUNOV FUNCTION V

The time derivative of the potential criterion V for the processes (a) and (b) in Fig. 1 may be found from the differential balance of entropy:

$$\sigma F \cdot dh + W \cdot S \pm W \cdot S_h = W(S + dS) \pm W(S_h + dS_h) \tag{11}$$

(the upper sign pertains to the concurrent reactor and the lower sign to the countercurrent reactor).

After simplification and using the relationship

$$\varepsilon \cdot \rho \cdot F \cdot dh/W \equiv dt \tag{12}$$

we obtain from equation (11):

$$\frac{\sigma}{\rho \cdot \varepsilon} = \frac{dS}{dt} \pm \frac{dS_h}{dt} = \frac{d\tilde{V}}{dt} \geq 0. \tag{13}$$

Because the entropy production, σ, is always non-negative it appears from equation (13) that the following entropy excess of the two-phase stream (taken in relation to the quasi-equilibrium)

$$\tilde{V} = S_M - S_M^0 \tag{14}$$

constitutes the appropriate criterion for the processes considered. Entropy S_M, appearing in equation (14), is computed as

$$S_M \equiv S \pm S_h \tag{15}$$

where signs + and − pertain to concurrent and countercurrent processes respectively.

Equation (13) may be transformed into more suitable form by substituting:

$$\frac{dS_h}{dt} = \frac{1}{T_h}\frac{di_h}{dt}, \tag{16}$$

$$\frac{dS}{dt} = \frac{1}{T}\frac{di}{dt} - \frac{\Delta\bar{\mu}}{M_C T}\frac{dw_C}{dt}, \tag{17}$$

$$\frac{di_h}{dt} = \mp\frac{di}{dt}\begin{pmatrix}-\text{ concurrent}\\ +\text{ countercurrent}\end{pmatrix}. \tag{18}$$

Thus we finally get the time derivative of the potential criterion $\tilde{V}$ in the form

$$\frac{d\tilde{V}}{dt} = \left(\frac{1}{T} - \frac{1}{T_h}\right)\frac{di}{dt} - \frac{\Delta\bar{\mu}}{M_C T}\frac{dw_C}{dt}, \tag{19}$$

which is common for both concurrent and countercurrent reactors.

In the calculations, section 4, the Liapunov function,

$$V = -(S_M - S_M^0), \tag{20}$$

was used which differed in sign from the function (14). Its total time derivative (a negative quantity)

$$\frac{dV}{dt} = -\left[\left(\frac{1}{T} - \frac{1}{T_h}\right)\frac{di}{dt} - \frac{\Delta\bar{\mu}}{M_C T}\frac{dw_C}{dt}\right] \leq 0 \tag{21}$$

was easily computed with the help of the thermodynamic relationship

$$\frac{di}{dt} = c_p\frac{dT}{dt} + \Delta\bar{H}M_C^{-1}\frac{dw_C}{dt} \tag{22}$$

as well as the state equations (2) and (3).

It is worth emphasizing that (just as for the processes without a chemical reaction [1]) the flow quantity S_M appears as the process potential of the flow systems considered. This quantity plays the same role as the "usual" entropy in the case of the closed, thermally isolated system. The time derivative of S_M in relation to the space time is identical to the adequate time derivative of the entropy after chronological time. This analogy is helpful when analyzing the thermodynamic properties of flow systems.

4. RESULTS FOR CONCURRENT AND COUNTERCURRENT PROCESSES

The results (obtained with the help of a computer) are presented in Figs. 2 and 3 which show the curves for the constant values of the Liapunov function V and its time derivative $\dot{V}$.

In the same diagrams the trajectories of the kinetic equations (2) and (3) are drawn. They are characterized by the same values of invariants (4)–(8) (and hence by the same singular point) but by different starting points. The computational data are taken from [3] and pertain to industrial synthesis of ammonia:

$$\tfrac{1}{2}N_2 + \tfrac{3}{2}H_2 = NH_3. \tag{23}$$

Methane and argon constitute the neutral component D. Concentrations at the inlet (in kmol kmol^{-1}) are: $W_{iH_2} = 0.6525$, $w_{iN_2} = 0.2715$, $w_{iNH_3} = 0.05$, $w_{iAr} = W_{iCH_4} = 0.04$.

The results correspond with the following reaction rate equation

$$r_C = 2 \cdot f_1 \cdot \exp\left(-\frac{E_1}{RT}\right)p^{1.5} \times y_A y_B^{1.5}\left[1 - \exp\left(\frac{2\Delta\bar{\mu}}{RT}\right)\right]\frac{1}{y_C} \tag{24}$$

where, according to [3],

$$E_1 = 87.152\,\text{kJ mol}^{-1}$$

$$f_1 = 7.498\,\text{kJ mol}^{-1}$$

$$p = 287\,\text{atm}.$$

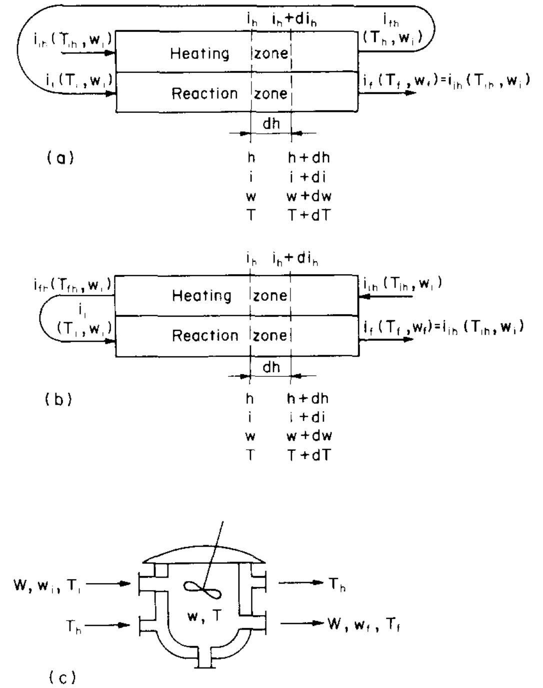

FIG. 1. Flow systems investigated: (a) concurrent reactor, (b) countercurrent reactor, (c) continuous flow stirred-tank reactor (CSTR).

The complete set of data may be found in [4].

Considering the direct relation between $\dot{V}$ and entropy source the time derivative of V is defined negatively. This means that the trajectories of the aforementioned processes should evolve toward the decreasing values of V. As is seen from Figs. 2 and 3 this is true for both concurrent and countercurrent reactors.

Some remarks should be made about V itself. In the case of the concurrent reactor V is positively defined. It is bowl-shaped with its minimum at the singular point (point 0 in Fig. 2). Comparing the signs of V and $\dot{V}$ it is possible to show the stability of the investigated family of trajectories using Liapunov's second theorem [2]. The course of the calculated trajectories confirms this conclusion; namely, that all the trajectories evolve in the direction of singular point creating a node.

In the case of the countercurrent reactor the surface of V has the shape of a saddle. The neighbourhood of the singular point (point 0 in Fig. 3) breaks up into regions in which the function has different signs. By Chetaev's theorem [2] it becomes possible to state the instability of the trajectories; this conclusion is confirmed by integrating the kinetic equations. From the diagram of the trajectories, Fig. 3, it is seen that only two characteristic trajectories (so called separatrices) can approach the singular point for $t \to +\infty$. All the remaining trajectories flow down through decreasing values of V towards its negative regions, omitting the singular point.

The results of [1] and this section indicate that for quasi-equilibrium singular points the Liapunov functions, constructed via thermodynamic approach, may constitute efficient criteria for the qualitative examination of the trajectories of heat and mass transfer processes occurring in non-reacting and reacting systems. Using such Liapunov functions it is possible to predict the direction of the trajectories' course, their stability, and, (in the case of saddles, Fig. 3) the position of the characterisitic trajectories separating the areas in which all trajectories have similar properties such as extrema of temperature or concentration of a valuable component. Such areas of similar properties have been marked in Fig. 3 with labels 1–4.

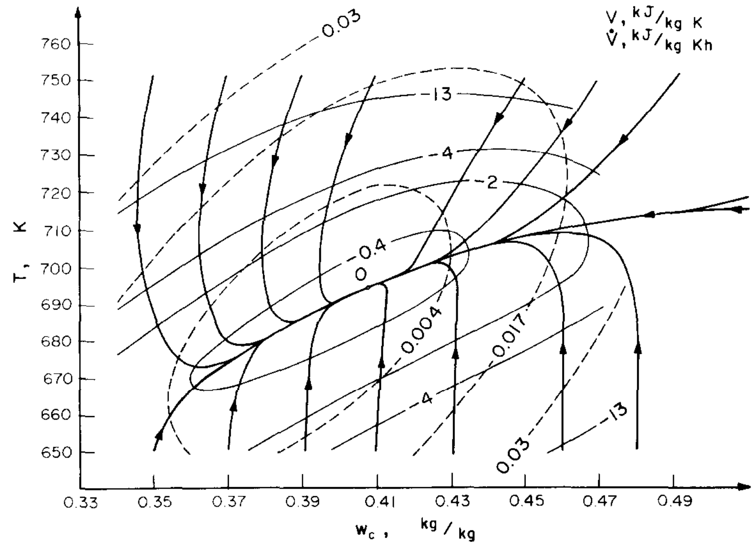

FIG. 2. Contours of Liapunov function V(– – – –), its time derivative $\dot{V}$(——) and trajectories (→—) for the process of exothermal synthesis in auto-thermal concurrent tubular reactor.

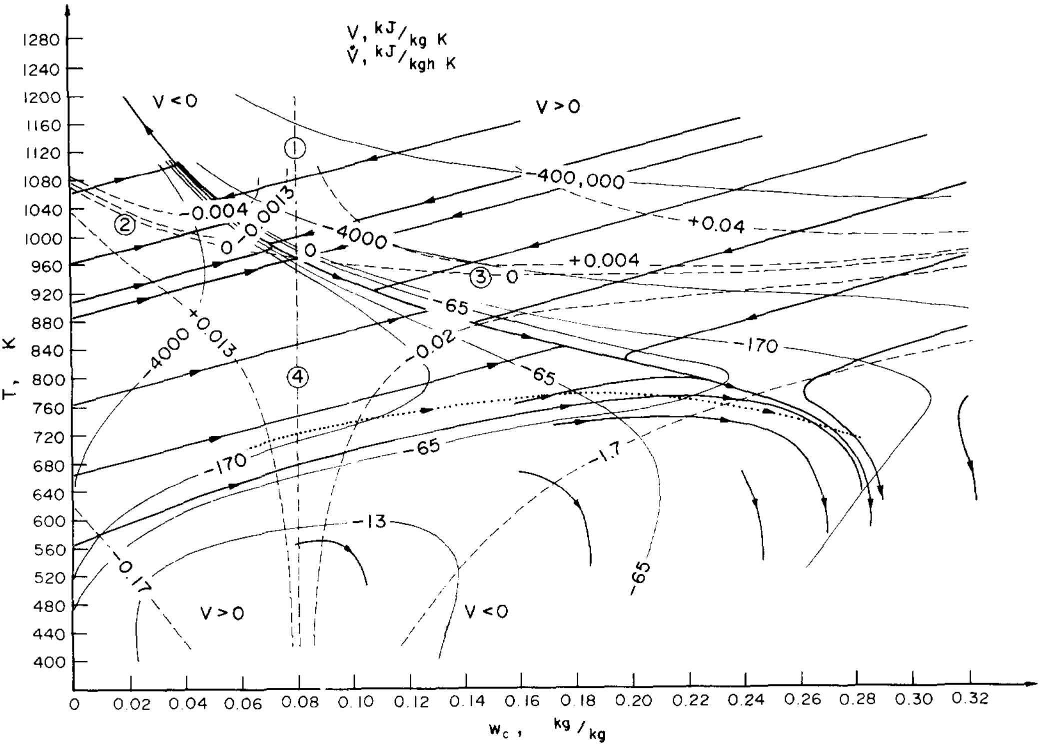

FIG. 3. Contours of Liapunov function V(----), its time derivative $\dot{V}$(——) and trajectories (→—) for the process of exothermal synthesis in auto-thermal countercurrent tubular reactor.

5. GENERAL REMARKS ABOUT PROCESSES WITH NON-EQUILIBRIUM SINGULAR POINT

When the singular point is the non-equilibrium stationary state, the entropy source becomes, as a rule, ineffective for constructing the potentials defining stability (or instability). This is because in such a stationary state the entropy source has a value greater than zero, while its excess in relation to the stationary state does not have a definite sign. In such cases therefore, the Liapunov functions must be constructed upon other principles, their time derivatives not being proportional to the entropy source.

It is generally known that the square forms of a defined sign can (although do not necessarily) constitute suitable Liapunov functions and lead to sufficient conditions of stability. Glansdorff and Prigo-

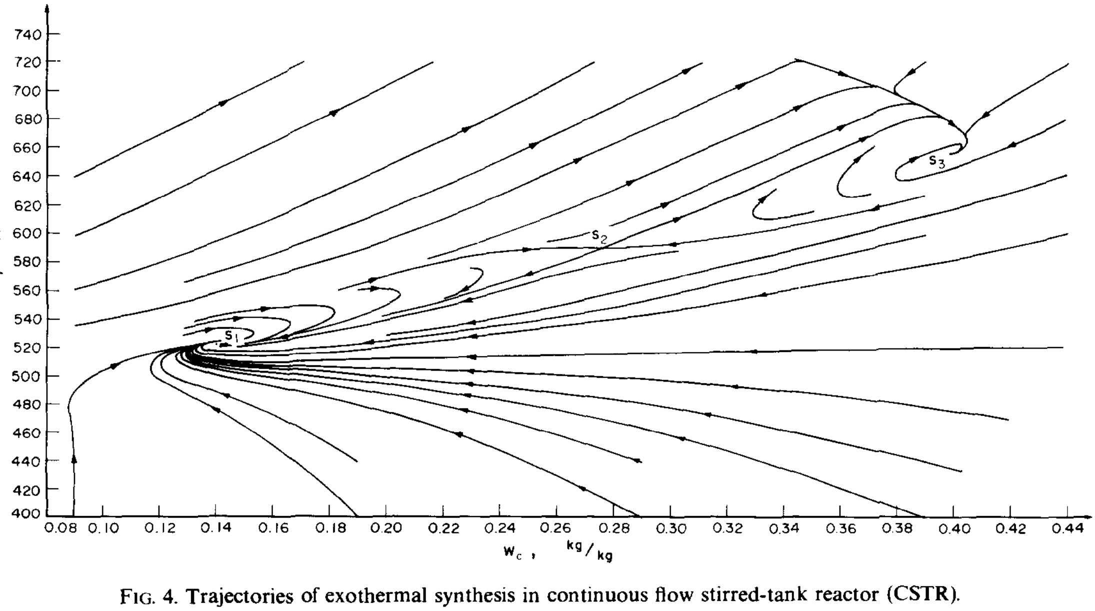

FIG. 4. Trajectories of exothermal synthesis in continuous flow stirred-tank reactor (CSTR).

gine [5] suggested the use of the 2nd differential of entropy, $\delta^2 S$, as the quantity criterion of this kind. As was verified in [6] this quantity is an efficient stability criterion when heat and/or mass transfer occurs in non-reacting systems.

However, it may happen (Section 6) that $\delta^2 S$ is not decisive about stability (or instability) when the transfer of heat or mass occurs together with the chemical reaction. Such a situation occurs only in the case of the stirred-tank reactor (CSTR) examined below. This is connected with the fact that the time derivative of $\delta^2 S$ loses the constant sign property during the transition from equilibrium to the stationary singular points. For this reason it will be necessary to look for another construction of the Liapunov function. Therefore in section 8 the construction of some generalized criterion function, V_s, defined as the sum of the thermodynamic function V and of some "kinetic term" is proposed. It will be shown that V_s can determine the stability where V or $\delta^2 S$ appear to fail.

6. INAPPROPRIATENESS OF THE PURELY THERMODYNAMIC LIAPUNOV FUNCTION V FOR CSTR

In the case of CSTR [Fig. 1, scheme (c)] the system evolution proceeds in chronological time, t, and the singular point is the non-equilibrium stationary state.

On the ground of the mass and energy balances we get the following dynamic model for CSTR in which reaction (1) occurs:

$$\frac{\mathrm{d}w_C}{\mathrm{d}t} = \frac{M_C \cdot r_C(T, w_C)}{\rho\varepsilon} + \frac{w_{iC} - w_C}{\theta}, \tag{25}$$

$$\frac{\mathrm{d}i}{\mathrm{d}t} = \frac{B}{\rho\varepsilon}(T_h - T) + \frac{i_i - i}{\theta}. \tag{26}$$

Energy equation (26) is equivalent to

$$\frac{\mathrm{d}T}{\mathrm{d}t} = \left[\frac{B}{\rho\varepsilon}(T_h - T) + \frac{i_i - i(T, w_C)}{\theta} - \frac{\mathrm{d}w_C}{\mathrm{d}t}\frac{\Delta H}{M_C}\right] c_p^{-1}. \tag{27}$$

Assuming again that the single reaction occurs, the remaining concentrations can be evaluated from equations (4)–(6).

It is possible to show [4] that the thermodynamic function,

$$V = i - i^0 - T^0(S - S^0) - \Delta\mu^0(w_C - w_C{}^0), \tag{28}$$

is positively defined while its square approximation is proportional to the well known non-positive quantity, the 2nd differential of the entropy [5]. This means that

$$V = -T^0 \Delta S_{\text{total}} = -\frac{1}{2} T^0 \delta^2 S \geqslant 0. \tag{29}$$

However, it has been verified that the time derivative of this function

$$\dot{V} = -T^0\left[\left(\frac{1}{T} - \frac{1}{T^0}\right)\frac{\mathrm{d}i}{\mathrm{d}t} - \left(\frac{\Delta\mu}{T} - \frac{\Delta\mu^0}{T^0}\right) M_C^{-1}\frac{\mathrm{d}w_C}{\mathrm{d}t}\right], \tag{30}$$

which, in the case of equilibrium or quasi-equilibrium, has a definite sign*, but in the examined process is not a function of definite sign. This indefiniteness of sign of (30) was confirmed by computations (Fig. 5); it is connected with the non-equilibrium nature of the singular point. In conection with that, neither V nor $\delta^2 S$ constitute an efficient criterion by means of which it is possible to decide the stability (Liapunov's second theorem) or instability (Chetaev's theorem) of the examined system.

8. CONSTRUCTION OF POTENTIAL V_s

It is useful to begin seeking a suitable Liapunov function, V_s, starting from constructing its time derivative as a function of definite sign.

Let us consider a linear model of n-coordinates of state x_i, which is obtained by linearization of the original non-linear model described by the original state variables X_i. The linearization is performed for the definite singular point $\mathbf{X}^0$ of the following non-linear system

$$\dot{\mathbf{X}} = f(\mathbf{X}). \tag{31}$$

The linearized model has the following vector-matrix form

$$\dot{\mathbf{x}} = \mathbf{A}\,\mathbf{x} \tag{32}$$

where $\mathbf{x} = \delta\mathbf{X}$ is the perturbation around X^0 as well as

$$\mathbf{A} = \left[\frac{\partial \dot{X}_i}{\partial X_k}\right]_{\mathbf{X}^0} = [a_{ik}].$$

We are looking for such a function V_s for which, from the definition

$$\dot{V}_s(\dot{\mathbf{x}}) \equiv a\dot{\mathbf{x}}\,\mathbf{B}\,\dot{\mathbf{x}} \tag{33}$$

where $\mathbf{B}$ is the symmetrical and positively defined matrix of the 2nd-order derivatives in the Taylor expansion of the thermodynamic function V, equation (28), evaluated at the singular point. As the 1st-order derivatives vanish at this point one has the square approximation:

$$V = -\frac{1}{2} T^0 \delta^2 S = \frac{1}{2}\mathbf{x}^{\mathrm{T}}\mathbf{B}\mathbf{x}. \tag{34}$$

All the elements of matrix $\mathbf{B}$ are known from the last equation. The constant coefficient a in equation (33) enables V_s to be of the same dimension as V.

Substitution of equation (32) into equation (33) gives:

$$\dot{V}_s(\mathbf{x}) = a\,(\mathbf{A}\,\mathbf{x})^{\mathrm{T}}\,\mathbf{B}\,\mathbf{A}\,\mathbf{x} = a\,\mathbf{x}^{\mathrm{T}}\,\mathbf{A}^{\mathrm{T}}\,\mathbf{B}\,\mathbf{A}\,\mathbf{x}. \tag{35}$$

As the system (32) is linear and the derivative $\dot{V}_s(\mathbf{x})$ a square quantity, the Liapunov function $V_s(\mathbf{x})$ must be of the square form, i.e.

$$V_s(\mathbf{x}) \equiv \frac{1}{2}\mathbf{x}^{\mathrm{T}}\,\mathbf{D}\,\mathbf{x}, \tag{36}$$

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*See inequality (21).

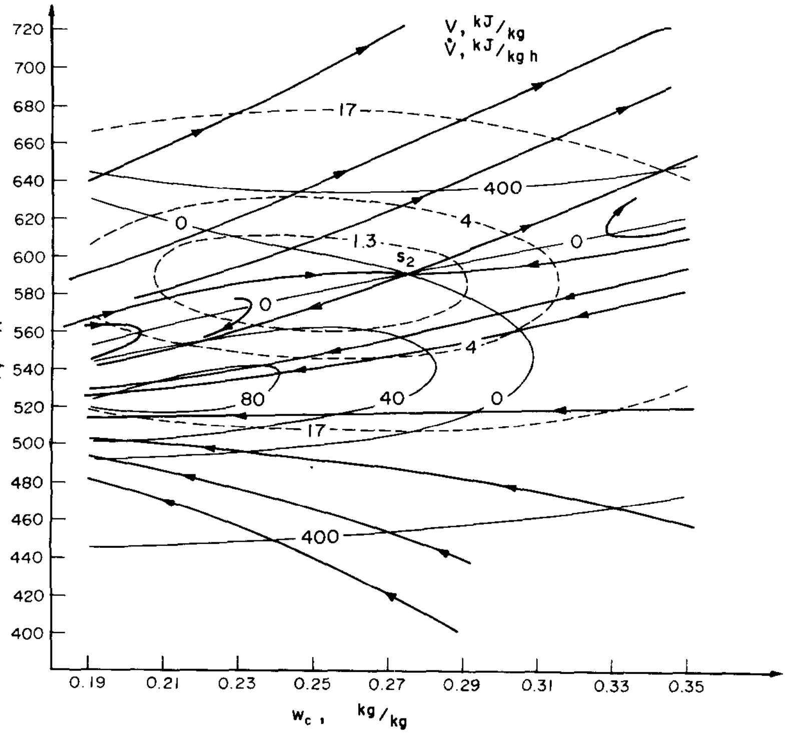

FIG. 5. Contours of thermostatic potential V(– – – –), its time derivative $\dot{V}$(——) and trajectories (→—) for exothermal synthesis in CSTR. Steady state S_2.

where **D** is an unknown symmetrical matrix, the elements of which must be found. Differentiation of equation (36) using equation (32) yields

$$\dot{V}_s(\mathbf{x}) = \frac{1}{2}\dot{\mathbf{x}}^T\mathbf{D}\,\mathbf{x} + \frac{1}{2}\mathbf{x}^T\,\mathbf{D}\,\dot{\mathbf{x}}$$

$$= \frac{1}{2}\mathbf{x}^T(\mathbf{A}^T\mathbf{D} + \mathbf{D}\,\mathbf{A})\mathbf{x}. \quad (37)$$

After comparing equations (35) and (37) we obtain the matrix equation

$$a\,\mathbf{A}^T\,\mathbf{B}\,\mathbf{A} = \frac{1}{2}(\mathbf{A}^T\,\mathbf{D} + \mathbf{D}\,\mathbf{A}), \quad (38)$$

where a, **A** and **B** are given. The solution of such equations is possible [7] and leads to the following result:

$$\mathbf{D} = f(\text{the elements of matrices } \mathbf{B} \text{ and } \mathbf{A}). \quad (39)$$

Putting the last result into equation (36) yields

$$V_s(\mathbf{x}) = \frac{1}{2}\mathbf{x}^T\,\mathbf{D}(b_{ik}, a_{ik})\mathbf{x}. \quad (40)$$

When equation (38) is solved, (40) becomes explicit and as such can be used for applications. The formula defines the square Liapunov function which may be used in the examination of global stability of the linear system (32). However the basic significance of this formula relies on the fact that it can also be used in the examination of the local stability (in a finite region) of the original non-linear system (31). For this purpose it becomes meaningful to separate out in (40) the thermostatic term [equations (28) and (34)]. We may write:

$$V_s(\mathbf{x}) = \frac{1}{2}\mathbf{x}^T(\mathbf{D} - \mathbf{B})\mathbf{x} + \frac{1}{2}\mathbf{x}^T\,\mathbf{D}\,\mathbf{x}. \quad (41)$$

Since equation (32) holds, the term $\mathbf{A}^{-1}\,\dot{\mathbf{x}}$ can be substituted instead of **x** into the first member of the right-hand side of equation (41). Then defining the "kinetic matrix" $\mathbf{K} = k_{ik}$ as

$$\mathbf{K} = \mathbf{A}^{-1T}(\mathbf{D} - \mathbf{B})\mathbf{A}^{-1} \quad (42)$$

the following potential criterion is obtained:

$$V_s(\mathbf{x}) = \frac{1}{2}\dot{\mathbf{x}}^T\,\mathbf{K}\,\dot{\mathbf{x}} + V(\mathbf{x}) \quad (43)$$

which is composed of the "kinetic" term (with **K**) and the "thermostatic" term $V(\mathbf{x})$ [equation (28)].

It is proposed that function (43) be treated as a generalization of (40) in the event of non-linear kinetic equations [see e.g. equations (25) (26) and (31)]. This generalization can be expressed in terms of the original (i.e. unperturbed) coordinates as

$$V_s(X_1 \ldots X_n) = \frac{1}{2}\sum_{i=1}\sum_{k=1} k_{ik}\frac{\mathrm{d}X_i}{\mathrm{d}t}\,\frac{\mathrm{d}X_k}{\mathrm{d}t}$$

$$+ V(X_1 \ldots X_n). \quad (44)$$

Application of equation (44) for the non-linear systems is connected with the substitution of the right-hand

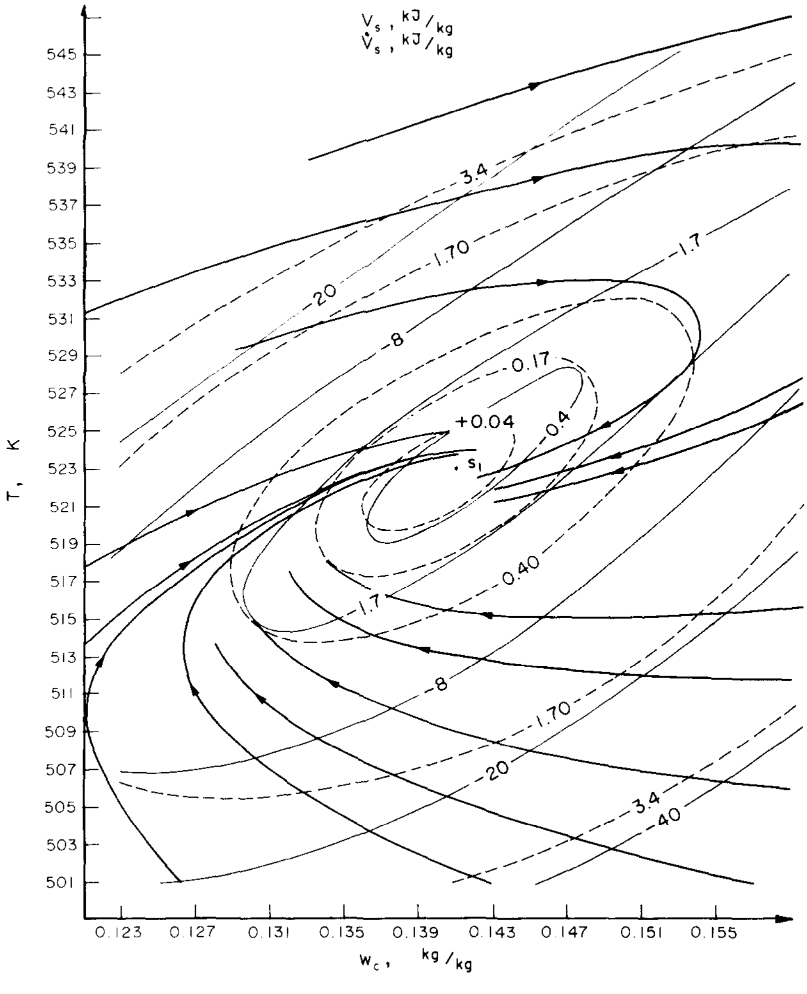

Fig. 6. Contours of the potential V_s(– – – –), its time derivative $\dot{V}_s$(——) and trajectories (→—) for exothermal synthesis in CSTR. Steady state S_1.

sides of the original state equations [c.f. equation (31)] instead of $\mathrm{d}X_i/\mathrm{d}t$ into equation (44), as well as with the generally non-square form V. Usually in thermodynamics V is an exergy (i.e. available energy) of the system with reference state T^0, μ_i^0. In the case of our CSTR the function V is described by equation (28).

It turns out [4] that when $n = 2$, the matrices **K** and **B** are proportional, as well as there being an explicit solution for k_{ik}. The complete analysis may be found in [4]; here we shall give only the final result:

$$\mathbf{K} = m\mathbf{B} = m\left[\frac{\partial^2 V}{\partial x_i \partial x_k}\right]_{-1} \tag{45}$$

where

$$m = (a_{11}a_{22} - a_{12}a_{21}) \tag{46}$$

The above formulae will now be applied to the CSTR considered in section 6. Assume that the exothermic reaction $\frac{1}{2}A + \frac{3}{2}B = C$ is, in presence of D, inert. The expanded form of the function V_s for our CSTR [state variables w_C and T, equations (25) and (27)] is:

$$V_s = \frac{1}{2}m\left[\left(\frac{\partial^2 V}{\partial T^2}\right)_{T^0, w_C^0}\left(\frac{\mathrm{d}T}{\mathrm{d}t}\right)^2 + 2\left(\frac{\partial^2 V}{\partial T \partial w_C}\right)_{T^0, w_C^0} \times \left(\frac{\mathrm{d}T}{\mathrm{d}t}\right)\left(\frac{\mathrm{d}w_C}{\mathrm{d}t}\right) + \left(\frac{\partial^2 V}{\partial w_C^2}\right)_{T^0, w_C^0}\left(\frac{\mathrm{d}w_C}{\mathrm{d}t}\right)^2\right] + V(T, w_C), \tag{47}$$

and its time derivative is [using equation (51)]

$$\dot{V}_s = m\left[\left(\frac{\partial^2 V}{\partial T^2}\right)_{T^0, w_C^0}\frac{\mathrm{d}T}{\mathrm{d}t}\left(\frac{\partial \dot{T}}{\partial T}\frac{\mathrm{d}T}{\mathrm{d}t} + \frac{\partial \dot{T}}{\partial w_C}\cdot\frac{\mathrm{d}w_C}{\mathrm{d}t}\right) + \left(\frac{\partial^2 V}{\partial w_C^2}\right)_{T^0, w_C^0}\frac{\mathrm{d}w_C}{\mathrm{d}t}\left(\frac{\partial \dot{w}_C}{\partial w_C}\cdot\frac{\mathrm{d}w_C}{\mathrm{d}t} + \frac{\partial \dot{w}_C}{\partial T}\cdot\frac{\partial T}{\mathrm{d}t}\right)\right] + \dot{V}(T, w_C). \tag{48}$$

As V is defined by equation (28), the elements of matrix **B** are:

$$\left(\frac{\partial^2 V}{\partial T^2}\right)_{T^0, w_C^0} = b_{11} = \frac{c_p^0}{T^0}, \tag{49}$$

$$\left(\frac{\partial^2 V}{\partial w_C^2}\right)_{T^0, w_C^0} = b_{22} = M_C^{-1}\left(\frac{\partial \Delta\mu_C}{\partial w_C}\right)_{T^0, w_C^0}, \tag{50}$$

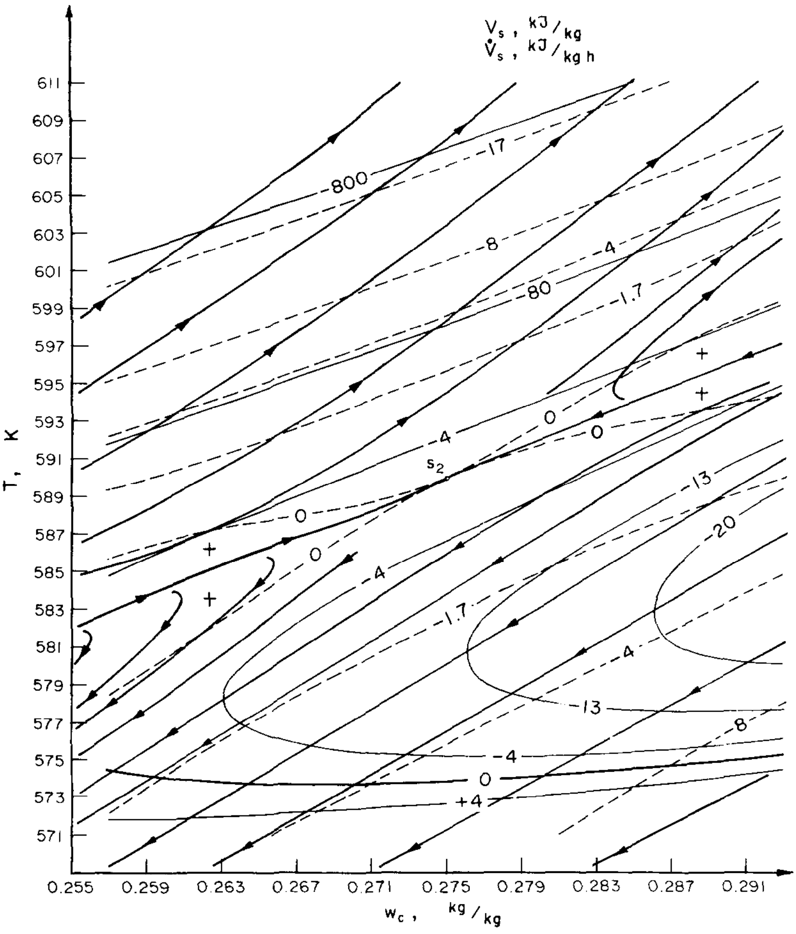

FIG. 7. Trajectories, V_s and $\dot{V}_s$ for CSTR. Steady state S_2.

$$\left(\frac{\partial^2 V}{\partial w_C \partial T}\right)_{T^0, w_C^0} = \left(\frac{\partial^2 V}{\partial T \partial w_C}\right)_{T^0, w_C^0} = b_{12} = b_{21} = 0. \qquad (51)$$

The coefficients a_{ik} are calculated by differentiating the left-hand sides of the dynamic equations (25) and (27), giving the derivatives:

$$a_{11} = \left(\frac{\partial \dot{T}}{\partial T}\right)_{T^0, w_C^0}; \quad a_{12} = \left(\frac{\partial \dot{T}}{\partial w_C}\right)_{T^0, w_C^0};$$

$$a_{21} = \left(\frac{\partial \dot{w}_C}{\partial T}\right)_{T^0, w_C^0}; \quad a_{22} = \left(\frac{\partial \dot{w}_C}{\partial w_C}\right)_{T^0, w_C^0}. \qquad (52)$$

This procedure leads to the computation of the coefficient m, equation (46), as well as of the "kinetic" matrix **K**, equation (45). Finally, it is possible to compute the function V_s and its time derivative $\dot{V}_s$ from formulas (47) and (48), respectively.

9. RESULTS OF CALCULATIONS FOR CSTR

It has been assumed that the area of heat exchange $F = 9.29\ \mathrm{m}^2$, the reactor volume $v_r = 2.83\ \mathrm{m}^3$, the coefficient of heat exchange $k = 102.4\ \mathrm{kJ/hm^2K}$ from which it resulted that $B = kF/v_r = 336\ \mathrm{kJ/hKm^3}$ in equation (27). Also it has been calculated that average residence time $\theta = 0.2333$ h, and the temperature of the inlet stream to the reactor $T_i = 694$ K. The reaction rate expression used had the structure of equation (24). The complete set of data is available in [4].

For the purpose of verifying the conclusions resulting from the analysis of the Liapunov functions, V and V_s, the trajectories of the process have been computed. They are shown in Fig. 4 in the surroundings of the three stationary states. It is easily seen that states S_1 and S_3 are stable and state S_2 is unstable.

We can now discuss the relation between the functions V, V_s and trajectories. In Fig. 5 there are trajectories shown in the vicinity of the second (unstable) stationary state S_2 as well as the curves for the constant values of the thermodynamic function V, equation (28), and its time derivative $\dot{V}$ in relation to equations (25) and (27). From the graph it appears that the time derivative $\dot{V}$ is not a function of definite sign and that there is no relation between the directions of increase (or decrease) of the function V and the mode of trajectory evolution. Non-effectiveness of V has also been observed in other cases, see [4]. As explained

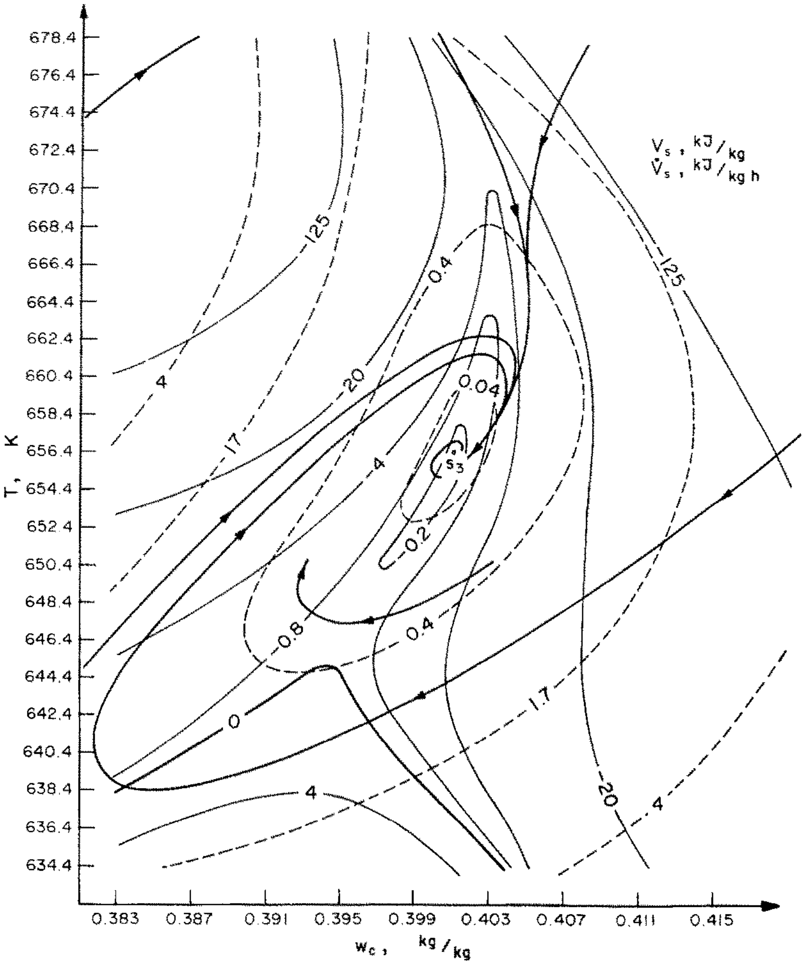

Fig. 8. Trajectories, V_s and $\dot{V}_s$ for CSTR. Steady state S_3.

earlier, it also means that the $\delta^2 S$ criterion fails in all these cases.

In the Figs. 6–8 the surroundings of the three stationary states, S_1, S_2 and S_3 are shown together with the curves for the constant value of the potential V_s and its time derivative $\dot{V}_s$. The curve $\dot{V}_s = 0$ is the boundary of the area of applicability of V_s. In the computations it has been stated that the function $\dot{V}_s$, in the surroundings of S_1–S_3 is negatively defined, i.e. the trajectories should always evolve in the direction of the decreasing values of V_s. From Figs. 6–8 it appears that it is so indeed; that means that V_s is really the potential of the examined non-linear process, in the region where $\dot{V}_s \leqslant 0$.

In Fig. 7 we have marked with a + the regions where the function V_s is positive. The only two trajectories, which aim at the state S_2 and separate the areas of stability of the stationary states S_1 and S_3 (cf. Fig. 4), must remain within the area $V_s > 0$. As may be seen in Fig. 7 such an effect takes place indeed, and this is an example of the effectiveness of function V_s in predicting the properties of trajectories.

The usefulness of V_s as the Liapunov criterion has also been verified for another, highly non-linear process of oxidation CO into CO_2 in which the limit cycle may occur [4].

The data presented in this article and in [1] indicate the considerable effectiveness of the Liapunov functions V and V_s in the investigation of stability and for predicting qualitative properties of trajectories of heat and mass transfer in both reacting and non-reacting systems.

The present approach makes it possible to classify and to systematize the trajectories according to common qualitative properties (e.g. according to extremes of concentrations or temperatures, type of stability, etc). Such properties may be discovered, in particular, with the aid of a systematic examination of the properties of the Liapunov functions V or V_s.

REFERENCES

1. S. Sieniutycz and J. Komorowska-Kulik, Thermodynamic approach to qualitative properties of trajectories of heat and mass transfer in gas–solid flow systems—I. Non-reacting systems, *Int. J. Heat Mass Transfer* **21**, 489–497 (1978).
2. B. P. Demidovich, *Mathematical Theory of Stability*. W.N.T., Warsaw (1972).

3. A. Murase, H. L. Roberts and A. D. Converse, Optimal thermal design of an autothermal ammonia synthesis reactor, *Ind. Engng. chem. Process Des. Devel.* **2**, 503–513 (1970).
4. J. Komorowska-Kulik, Thermodynamic Liapunov's functions and trajectories of heat and mass transfer processes in gas–solid systems. PhD thesis, Inst. of Chem. Engng, Warsaw Tech. Univ. (1979).
5. P. Glansdorff and I. Prigogine, *Thermodynamic Theory of Structure Stability and Fluctuations*. Wiley–Interscience, New York (1971).
6. E. Winkiel, Thermodynamic analysis and linear problems of stability for dryers and reactors. MsD thesis, Inst. of Chem. Engng, Warsaw Tech. Univ. (1976).
7. E. A. Barabaszyn, *Liapunov functions*. Science, Moscow (1970).

APPROCHE THERMODYNAMIQUE DES PROPRIETES QUALITATIVES DES TRAJECTOIRES DE TRANSFERT DE CHALEUR ET DE MASSE DANS LES SYSTEMES D'ECOULEMENT GAZ–SOLIDE—II. SYSTEMES REACTIFS

Résumé—Cet article constitue la seconde partie du travail initié dans [1]. On étudie les propriétés qualitatives et la stabilité des trajectoires des transferts simultanés de chaleur et de masse dans des systèmes réactifs en écoulement. Pour ces systèmes dans lesquels le point singulier est du type de quasi équilibre, la fonction thermodynamique de Liapunov V, qui résulte du bilan entropique, est un critère efficace de stabilité ou d'instabilité. Tandis que dans le cas d'un point singulier de non équilibre stationnaire une fonction générale V_s, définie comme la somme de V et d'un terme "cinétique" convient pour la prévision des propriétés qualitative et la stabilité des trajectories.

THERMODYNAMISCHE BEHANDLUNG DER QUALITATIVEN EIGENSCHAFTEN VON TRAJEKTORIEN BEI WÄRME- UND STOFFÜBERTRAGUNG IN GAS–FESTSTOFF-SYSTEMEN—II. REAGIERENDE SYSTEME

Zusammenfassung—Dieser Artikel beschreibt den zweiten Teil der in [1] begonnenen Arbeit. Es werden die qualitativen Eigenschaften und die Stabilität von Trajektorien bei simultanen Wärme- und Stoffübertragungsprozessen in reagierenden Strömungen untersucht. Für jene Systeme, deren Singularität vom Quasi-Gleichgewichtstyp ist, bildet die thermodynamische Liapunov-Funktion V, die aus der Entropiebilanz resultiert, ein brauchbares Stabilitäts- oder Instabilitätskriterium. Im Fall einer stationären Singularität im Ungleichgewicht reicht eine verallgemeinerte Funktion V_s, definiert als Summe von V und einigen "kinetischen" Termen zur Berechnung der qualitativen Eigenschaften und Stabilität von Trajektorien aus.

ТЕРМОДИНАМИЧЕСКОЕ ОПИСАНИЕ КАЧЕСТВЕННЫХ ХАРАКТЕРИСТИК ТРАЕКТОРИЙ ТЕПЛО- И МАССОПЕРЕНОСА В СИСТЕМАХ ГАЗОВЫЙ ПОТОК — ТВЕРДОЕ ТЕЛО — II. РЕАГИРУЮЩИЕ СИСТЕМЫ

Аннотация — Статья является продолжением ранее опубликованной работы [1]. Исследуются качественных характеристики и устойчивость траекторий совместного тепло- и массопереноса в реагирующих проточных системах. Для систем с квазиравновесной сингулярной точкой критерием эффективной устойчивости (или неустойчивости) может служить термодинамическая функция Ляпунова V, определяемая на основе баланса энтропий. В случае же стационарной неравновесной сингулярной точки для расчета качественных характеристик траекторий удобна функция более общего вида V_s, определяемая как сумма V и некоторого «кинетического» слагаемого.