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

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Abstract—Study is made of qualitative properties and stability of trajectories of simultaneous heat- and mass-transfer processes in gas–solid flow systems.

Liapunov functions based on the thermodynamic principle are constructed, and instability of trajectories of counter flow processes is thermodynamically grounded. Emphasis is made on a general character of the above thermodynamic approach to the stability and qualitative properties of trajectories.

NOMENCLATURE

a,	solid specific surface $[\text{m}^2\,\text{m}^{-3}]$;
C, C^0,	invariant of the process and its numerical value, respectively;
G,	dry gas flow rate per unit apparatus cross-sectional area, $G/S \equiv Q$ $[\text{kg}\,\text{m}^{-2}\cdot\text{s}^{-1}]$;
h,	apparatus height [m];
i_g, i_g^0,	gas flow enthalpy per unit dry gas mass and gas enthalpy at a singular point, respectively $[\text{J}\,\text{kg}^{-1}]$;
i_s,	gas enthalpy in equilibrium with solid $[\text{J}\,\text{kg}^{-1}]$;
$i_{\omega s}$,	moisture enthalpy in gas phase $[\text{J}\,\text{kg}^{-1}]$;
i_{ps},	moisture enthalpy in vapour state in equilibrium with solid $[\text{J}\,\text{kg}^{-1}]$;
I_s, I_s^0,	solid enthalpy per unit mass of dry substance in any state and at singular point, respectively $[\text{J}\,\text{kg}^{-1}]$;
K'_g,	mass-transfer coefficient related to driving force, X_g–X_s $[\text{kg}\,\text{m}^{-2}\cdot\text{s}^{-1}]$;
Le,	Lewis factor;
m,	mass per unit mass of dry substance $[\text{kg}\,\text{kg}^{-1}]$;
$\tilde{Q}$,	heat per unit mass of dry substance $[\text{J}\,\text{kg}^{-1}]$;
s_m, s_g,	two-phase flow entropy and gas entropy, respectively $[\text{J}\,\text{K}^{-1}\,\text{kg}^{-1}]$;
S_s,	solid entropy per unit mass of dry substance $[\text{J}\,\text{K}^{-1}\,\text{kg}^{-1}]$;
S,	dry solid flow rate per unit apparatus cross-sectional area $[\text{kg}\,\text{m}^{-2}\cdot\text{s}^{-1}]$;
T_g, t_g,	gas temperature [K, °C];
T^0, T^{ot},	temperature at a singular point and temperature of environment [K];
T_s, t_s,	solid temperature [K, °C];
V, $\dot{V}$,	Liapunov function and its time derivative $[\text{J}\,\text{kg}^{-1}]$; $[\text{kcal}\,\text{kg}^{-1}]$;
W_s, W_s^0,	absolute moisture content of solid in any state and at a singular point, respectively $[\text{kg}\,\text{kg}^{-1}]$ or $[\text{g}\,\text{kg}^{-1}]$;
X_g, X_s,	absolute gas humidity in any state and in equilibrium with solid, respectively;
$x_1, x_2 \ldots x_r$,	coordinates of state vector;
α,	heat-transfer coefficient $[\text{J}\,\text{K}^{-1}\cdot\text{m}^2\cdot\text{s}]$;
μ_ω, μ_ω^0,	chemical potential of moisture in any state and at a singular point, respectively $[\text{J}\,\text{kg}^{-1}]$;
τ,	dimensionless time.

Superscripts

0,	singular point;
ot,	environment.

Subscripts

g,	gas;
s,	solid;
m,	mean flows;
ω,	moisture;
ωg, ωs,	moisture in gas and solid phase, respectively.

1. INTRODUCTION

In many processes the coupling between heat and mass transfer frequently hampers even approximate forecast of qualitative properties of process trajectories. Successive mathematical study of such properties allows analysis of possible trajectories and their relations.

The present paper is concerned with the thermodynamic approach to the trajectory stability with a reference to steady adsorption and drying of granular substance in one-dimensional adiabatic or non-adiabatic flow systems involving co-, counter- and

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cross-flows. However, it should be mentioned here that this approach will also be applied to no less important processes (for example, those with chemical reactions).

With regard to the one-dimensionality and steadiness of the flow processes under consideration, their mathematical model is a set of ordinary differential equations. The stability and qualitative properties of trajectories are analyzed around one point, which is called singular and is characterized by a zero rate of a change in the process state. The process at a singular point is steady, equilibrium or quasi-equilibrium. This paper deals only with those flow processes, in which a singular state represents thermodynamic quasi-equilibrium between two phases (a "quasi-equilibrium state" is attributed to a small amount of dissipated heat due to slip of two phases).

If trajectories of a process are stable, then slight changes in the initial conditions result in small variations of trajectories. In an unstable process, minor changes in the initial conditions (disturbances) will grow indefinitely in our space time τ.

2. METHOD

For the stability cases investigated here, the second Liapunov technique as applied to analyzing the properties of some state function and its absolute derivative, gives interesting physical results. However, there are, as a rule, difficulties, associated with constructing a Liapunov function.

In the present paper the examples of flow processes will illustrate how to construct Liapunov functions and how physical interpretation of the Liapunov function is incorporated with that of the invariants of equations for a given process. Owing to this fact, the Liapunov function will be sought as an excess value of some potential, found in terms of the thermodynamic approach, in relation to its magnitude in the quasi-equilbrium state [1].

Since this approach can be applied to other processes, an attempt is made here to develop the stability theory as general as possible. This theory employs the so-called invariants of a process* and will be analyzed in detail in the next section. It should be noted that the study of singular-state stability of a thermodynamic system and that of a mechanical system has much in common, the latter being done by the known Routh method [2] "reduction of coordinates".

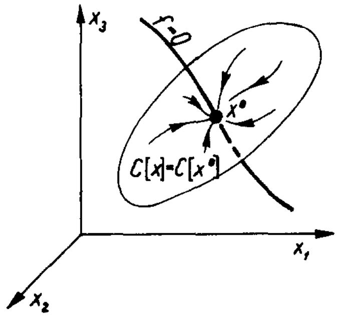

FIG. 1. A trajectory subclass in the state space, $r = 3$, $k = 1$. Evolution in space time τ is considered.

3. INVARIANTS AND REDUCTION OF COORDINATES

Study will be made of a process described by the following set of r-differential equations†:

$$\frac{dx_1}{d\tau} = f_1[x_1, x_2 \dots x_n \dots x_r]$$

$$\frac{dx_2}{d\tau} = f_2[x_1, x_2 \dots x_n \dots x_r]$$

$$\vdots$$

$$\frac{dx_n}{d\tau} = f_n[x_1, x_2 \dots x_n \dots x_r]$$

$$\vdots$$

$$\frac{dx_r}{d\tau} = f_r[x_1, x_2 \dots x_n \dots x_r]. \tag{1}$$

The nature of the processes investigated* is such (Figs. 1, 2) that set (1) is characterized by some variety of $k = r - n$ – dimensionality in a state space (where r is the number of equations and n is the dimensionality of a hypersurface, on which there exist trajectories belonging to a given singular point). The numbers r, k and n satisfy $n \leqslant r$ and $k \geqslant 0$. On the variety of $k = r - n$ dimensionality, the velocities, i.e. functions $f_1 f_2 \dots f_n \dots f_r$, are identically equal to zero. This variety is the equilibrium $k = r - n$ dimensional surface. The equation for such a surface is found by equating the RHS of (1) to zero. Solution to the stability problem is associated with studying a process trajectory at a prescribed point x^0 $(x_1^0, x_2^0, \dots x_n^0 \dots x_r^0)$ on the variety $f_1 = f_2 \dots = f_n = \dots f_r = 0$.

Note that a certain point x^0 (Fig. 1) may be achieved only via a subclass of trajectories characterized by the predicted values of process invariants. The number of invariants is $k = r - n$, i.e. equals the equilibrium surface dimensionality, and their equations assume the form:

$$\begin{aligned} &C_{n+1}[x_1, x_2 \dots x_n \dots x_r] \\ &\qquad = C_{n+1}[x_1^0, x_2^0 \dots x_n^0 \dots x_r^0] = C_{n+1}^0 \\ &C_{n+2}[x_1, x_2 \dots x_n \dots x_r] \\ &\qquad = C_{n+2}[x_1^0, x_2^0 \dots x_n^0 \dots x_r^0] = C_{n+2}^0 \\ &C_r[x_1, x_2 \dots x_n \dots x_r] \\ &\qquad = C_r[x_1^0, x_2^0 \dots x_n^0 \dots x_r^0] = C_r^0. \end{aligned} \tag{2}$$

If equations (2) for invariants $C_{n+1}, C_{n+2} \dots C_r$ are known, then the values of $C_{n+1}^0, C_{n+2}^0 \dots C_r^0$ corresponding to a given singular point x_0 may be numerically found.

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*For example, for some batch chemical isothermal reactions the invariants are: volume, temperature, some mole combinations of reaction stechiometry, as well as inert species moles.

†In the equations, brackets [ ] and { } denote a functional relation and brackets ( ) – multiplication.

*See, also Section 5.

This procedure will be called prediction of values of $C_{n+1}, C_{n+2}, \ldots C_r$ at the appropriate level. Then, a set of equations (1) should be transformed from variables $x_1 x_2 \ldots x_n \ldots x_r$ to variables $x_1 x_2, \ldots x_n, C_{n+1} \ldots C_r$. Since $k = r-n$ invariants are present, the number of non-trivial coordinates will be reduced to n. As a result a set of equations (1) takes the form:

$$\frac{dC_{n+1}}{d\tau} = 0$$

$$\frac{dC_r}{d\tau} = 0 \qquad (3)$$

$$\frac{dx_1}{d\tau} = g_1[x_1 \ldots x_n, C_{n+1} \ldots C_r]$$

$$\frac{dx_n}{d\tau} = g_2[x_1 \ldots x_n, C_{n+1} \ldots C_r]. \qquad (4)$$

Prediction of the parameters $C_{n+1}, \ldots C_r$ in equations (4) at the appropriate level $(C^0_{n+1} \ldots C^0_r)$ isolates from a trajectory family in set (1) only a trajectory subclass satisfying a point $(x^0_1, x^0_2 \ldots x^0_n \ldots x^0_r)$, relative to which the trajectory stability is examined.

The invariant concept discussed here should be associated with the available theorems of the stability theory which will be considered in brief below.

The statement of the stability problem allows alternatively determination not of the coordinates of a point $(x^0_1, x^0_2 \ldots x^0_n \ldots x^0_r)$ but of numerical values of $C_{n+1} \ldots C_r$. The singular-point position is uniquely found by prescribing constant $C^0_{n+1} \ldots C^0_r$. The first n-coordinates of this point are obtained by setting the RHS of equations (4) at $C = C^0$ to zero and by solving the appropriate set of the equations. The remaining coordinates follow from (2).

4. THEOREMS OF STABILITY AND INSTABILITY

4.1. *Liapunov's first theorem* [3]

If there exists a positive scalar function $V[x_1, x_2 \ldots x_n, C^0_{n+1} \ldots C^0_r]$ with a negative derivative $\dot{V}[x_1, x_2 \ldots x_n, C^0_{n+1} \ldots C^0_r]$ adjoint with set (4) where $C_{n+1} = C^0_{n+1} \ldots C_r = C^0_r$, then the trivial solution for $x^0 = (x^0_1, x^0_2 \ldots x^0_n)$, is stable (after Liapunov) at $\tau \to \infty$.

4.2. *Chetaev's formula for instability* [3]

If for the set of equations (1) there exists a function satisfying the conditions: (a) for any large values of τ at any singular point $(x^0_1, x^0_2 \ldots x^0_n)$ there is a domain, in which the function V and its time derivative $\dot{V}$ have the same sign, (b) in this domain, the function V is restrictive and its derivative $\dot{V}$ has a constant sign around a singular point, then the trivial solution to this set is unstable.

5. DIFFERENTIAL EQUATIONS

Drying and moistening processes of solid (Fig. 2) are investigated assuming that these are isobaric, and heat exchange occurs only between a gas phase and environment. The gas flow may be co- and countercurrent. (The case of one-dimensional cross-flow will be analyzed, in brief, later on, as it proceeds from these considerations.)

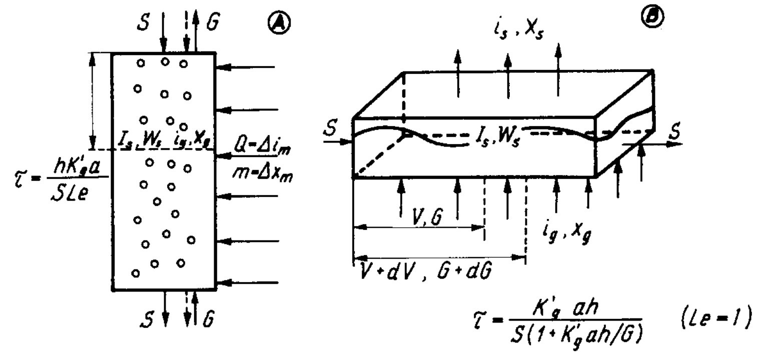

FIG. 2. A schematic drawing of the systems under study.

First, derive equations for adiabatic processes. Energy and mass balance for an arbitrary cross-sectional apparatus area yields:

$$\pm G di_g = S dI_s = \{\alpha(t_g - t_s) + i_{ps} K'_g (X_g - X_s)\} adh, \qquad (5, 6)$$

$$\pm G dX_g = S dW_s = K'_g (X_g - X_s) adh. \qquad (7, 8)$$

(the upper sign stands for concurrent flow and the lower for counterflow).

Enthalpies and concentrations were applied to describe a process, so the kinetic term in equation (6) should be expressed as a function of appropriate enthalpy and moisture content of a gas. For this purpose the equation

$$i_g - i_s = C_g(t_g - t_s) + i_{ps}(X_g - X_s) \qquad (9)$$

is used in equation (6).

As a result we have:

$$\pm G di_g = S dI_s = \frac{\alpha}{C_g}\left[i_g - i_s + i_{ps} \times \left(\frac{C_g K'_g}{\alpha} - 1\right)(X_g - X_s)\right] adh. \qquad (10, 11)$$

The determination of the following dimensionless quantities: $Le \equiv K'_g C_g/\alpha$ (Lewis number); $Q \equiv \pm G/S$ (dimensionless ratio for co- and countercurrent flow);

$\tau \equiv hK'_g a/SLe$ (dimensionless residence time of solid) yields a set of differential equations for an adiabatic process resulting from equations (10), (11), (7) and (8):

$$\frac{\mathrm{d}I_s}{\mathrm{d}\tau} = i_g - i_s[I_s, W_s] + (Le-1)i_{ps}[I_s, W_s](X_g - X_s[I_s, W_s]) \tag{12}$$

$$\frac{\mathrm{d}W_s}{\mathrm{d}\tau} = X_g - X_s[I_s, W_s] \tag{13}$$

$$\frac{\mathrm{d}i_g}{\mathrm{d}\tau} = -\{i_g - i_s[I_s, W_s] + (Le-1)i_{ps}[I_s, W_s](X_g - X_s[I_s, W_s])\}Q^{-1} \tag{14}$$

$$\frac{\mathrm{d}X_g}{\mathrm{d}\tau} = -(X_g - X_s[X_s, W_s])Q^{-1}, \tag{15}$$

where the functions $X_s[I_s, W_s]$ and $i_s[I_s, W_s]$ describe the equilibrium of a gas–solid system. For non-adiabatic systems which will be considered below, equations (12) and (13) are also valid because there is no heat exchange between solid and environment.

Quantities i_g, I_s, X_g and W_s are state coordinates in equations (12)–(15). Proceeding from these equations or from the law of conservation of energy and mass of adiabatic process, it follows that the invariants of the set of the equations analyzed are the functions:

$$i_m[i_g, I_s] = Qi_g + I_s = Qi_g^0 + I_s^0 \qquad (i_g^0 \equiv i_s[I_s^0, W_s^0]), \tag{16, 17}$$

$$X_m[X_g, W_s] = QX_g + W_s = QX_g^0 + W_s^0 \qquad (X_g^0 \equiv X_s[I_s^0, W_s^0]) \tag{18, 19}$$

for mean enthalpy and moisture content of a two-phase jet per dry solid flow rate.

The use of the invariants i_m, X_m in equations (12)–(13) allows the number of state coordinates to be reduced to two and a set of differential equations with the parameters [set (4)] to be obtained:

$$\frac{\mathrm{d}I_s}{\mathrm{d}\tau} = \frac{i_m - I_s}{Q} - i_s[I_s, W_s] + (Le-1)i_{ps}[I_s, W_s]\left(\frac{X_m - W_s}{Q} - X_s[I_s, W_s]\right) \tag{20}$$

$$\frac{\mathrm{d}W_s}{\mathrm{d}\tau} = \frac{X_m - W_s}{Q} - X_s[I_s, W_s]. \tag{21}$$

For adiabatic process involving no external mass transfer, $i_m = i_m^0$, $X_m = X_m^0$ where i_m^0, X_m^0 are the predicted invariant values at the appropriate level. For i_m, X_m to be determined at some singular point I_s^0, W_s^0, it is necessary to calculate equilibrium coordinates $i_g^0 = i_s[I_s^0, W_s^0]$, $X_g^0 = X_s[I_s^0, W_s^0]$, see [4], and to find numerical values of the invariants from equations (17) and (19).

Substitutions of i_m^0 and X_m^0 into state equation (20)–(21) gives the equations which satisfy a predetermined singular point (I_s^0, W_s^0). Invariants, more than other physical quantities, are important for physical characteristics of any process. Therefore, based on physical and chemical considerations, a set of equations (3)–(4) is very often obtained, but not that of equations (1), although the latter is less particular.

To illustrate the cases, in which the use of the kinetic equations in the form of (1) is inefficient, non-adiabatic adsorption and drying processes will be discussed below. The first case considers a process with no external mass transfer (X_m = constant) but with such heat transfer that mean entropy of a two-phase jet remains constant:

$$s_m = Qs_g + S_s = Qs_g^0 + S_s^0. \tag{22, 23}$$

The employment of invariants, equations (18) and (22), in the analytical expression representing gas enthalpy as a function $i_g[s_g, X_g]$ yields:

$$i_g[s_m, X_m, I_s, W_s] = i_g\left[\frac{s_m - S_s[I_s, W_s]}{Q}, \frac{X_m - W_s}{Q}\right]. \tag{24}$$

Substitution of formula (24) into equation (12) gives an equation

$$\frac{\mathrm{d}I_s}{\mathrm{d}\tau} = i_g\left[\frac{s_m - S_s[I_s, W_s]}{Q}, \frac{X_m - W_s}{Q}\right] - i_s[I_s, W_s] + (Le-1)i_{ps}[I_s, W_s] \times \left(\frac{X_m - W_s}{Q} - X_s[I_s, W_s]\right). \tag{25}$$

which, together with equation (21), describes kinetics of an isoentropic process.

Of considerable practical interest is another non-adiabatic process, in which heat transfer provides temperature constancy of a gas phase. Equation (19) and the equation

$$T_g = T^0 \qquad (T^0 \equiv T_s^0[I_s^0, W_s^0]) \tag{26}$$

describe invariants of a process.

A set of the kinetic equations [of type (4)] now consists of equation (21) and energy equation (12), in which gas enthalpy is expressed as a function of variables T_g, X_m, I_s, W_s;

$$\frac{\mathrm{d}I_s}{\mathrm{d}\tau} = i_g\left[T_g, \frac{X_m - W_s}{Q}\right] - i_s[I_s, W_s] + (Le-1)i_{ps}[I_s, W_s]\left(\frac{X_m - W_s}{Q} - X_s[I_s, W_s]\right), \tag{27}$$

where $T_g = T^0$ and $X_m = X_m^0$ are the calculated invariants, respectively.

The last case to be discussed deals with constant parameters of a gas phase. Any two variables characterizing, for example, a gas state, i_g and X_g, serve as process invariants. At some singular point I_s^0, W_s^0, the invariants of a process are described by:

$$i_g = i_g^0 \qquad (i_g^0 = i_s[I_s^0, W_s^0]) \tag{28}$$

$$X_g = X_g^0 \qquad (X_g^0 = X_s[I_s^0, W_s^0]) \tag{29}$$

and the set of the equations of type (4) includes equations (12) and (13), which account for relations (28) and (29).

It may be shown that with appropriate replacement of a time variable, τ, set (12)–(13) yields, at $Le = 1$, equations which describe a one-dimensional cross-flow process in a horizontal fluidized exchanger {see equations (22) and (23) from [5]}. This allows study of the stability of one-dimensional cross-flow using equations (12) and (13) at $Le = 1$.

Since a parameter Q is absent in equations (12) and (13) and $i_g = i_g^0$, and $X_g = X_g^0$, then in this case set (12), (13), (28) and (29) is identical for co- and countercurrent flows.

6. STABILITY CRITERION

6.1. *Thermodynamic consideration*

The most general case is concerned with a non-adiabatic system, in which not only heat but also moisture exchange between a gas phase and environment occurs (Fig. 2). The second and first laws of thermodynamics yields:

$$\mathrm{d}(S_s+Qs_g) \geqslant \frac{\mathrm{d}\tilde{Q}}{T_g} + s_{\omega g}\mathrm{d}(W_s+QX_g), \tag{30}$$

$$\mathrm{d}\tilde{Q} = \mathrm{d}(I_s+Qi_g) - i_{\omega g}\mathrm{d}(W_s+QX_g). \tag{31}$$

Eliminating a differential $\mathrm{d}\tilde{Q}$ from equations (30) and (31) and reminding that

$$\mu_{\omega g} = i_{\omega g} - T_g s_{\omega g} \tag{32}$$

and that $\mathrm{d}\tau > 0$, we have:

$$\frac{\mathrm{d}(I_s+Qi_g)}{\mathrm{d}\tau} - T_g\frac{\mathrm{d}(S_s+Qs_g)}{\mathrm{d}\tau} - \mu_{\omega g}\frac{\mathrm{d}(W_s+QX_g)}{\mathrm{d}\tau} \leqslant 0. \tag{33}$$

Substitution of entropy differentials (P = constant)

$$\mathrm{d}S_s = \frac{\mathrm{d}I_s - \mu_{\omega s}\mathrm{d}W_s}{T_s}, \tag{34}$$

$$\mathrm{d}s_g = \frac{\mathrm{d}i_g - \mu_{\omega g}\mathrm{d}X_g}{T_g} \tag{35}$$

into equation (33) results in an alternative form of inequality (33):

$$T_g\left\{\left(\frac{1}{T_g} - \frac{1}{T_s}\right)\frac{\mathrm{d}I_s}{\mathrm{d}\tau} + \left(\frac{\mu_{\omega s}}{T_s} - \frac{\mu_{\omega g}}{T_g}\right)\frac{\mathrm{d}W_s}{\mathrm{d}\tau}\right\} \leqslant 0. \tag{36}$$

6.2. *Liapunov function*

For an adiabatic system, $i_m = i_m^0$, $X_m = X_m^0$. The employment of formulae (16)–(19) in inequality (33) and allowance for $T_g > 0$ give:

$$\frac{\mathrm{d}}{\mathrm{d}\tau}\left\{-S_s[I_s, W_s] - Qs_g\left[\frac{i_m^0 - I_s}{Q}, \frac{X_m - W_s}{Q}\right]\right\} \leqslant 0. \tag{37}$$

Formula (37) shows that mean gas-suspension entropy with an opposite sign is a potential of an adiabatic flow process. The Liapunov function should be zero in a singular state and is consequently defined by:

$$V[I_s, W_s, i_m^0, X_m^0] = s_m[I_s^0, W_s^0, i_m^0, X_m^0] - s_m[I_s, W_s, i_m, X_m], \quad (s_m \equiv S_s + Qs_g). \tag{38}$$

For a quantitative comparison of dissipation in adiabatic and nonadiabatic systems, more preferable is another form of the Liapunov function for an adiabatic system. The Liapunov function in such a form represents a change in exergy (available energy) of a thermodynamic system described by the formula following from the Gouya–Stodola law [6]:

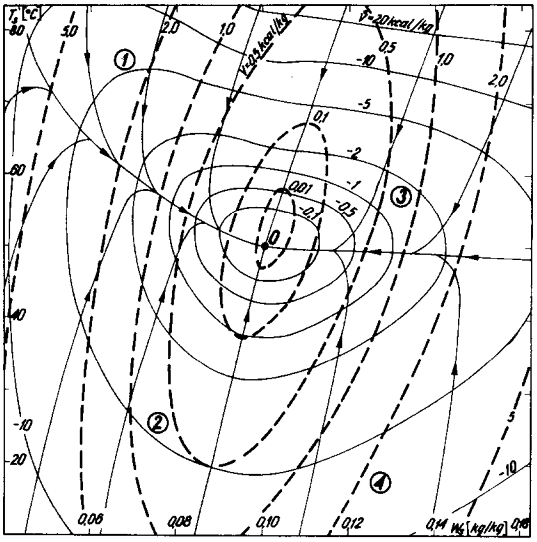

FIG. 3. Lines of constant values of functions V and $\dot{V}$ and trajectories. Adiabatic cocurrent flow process, $Q = 2$, $Le = 1$.

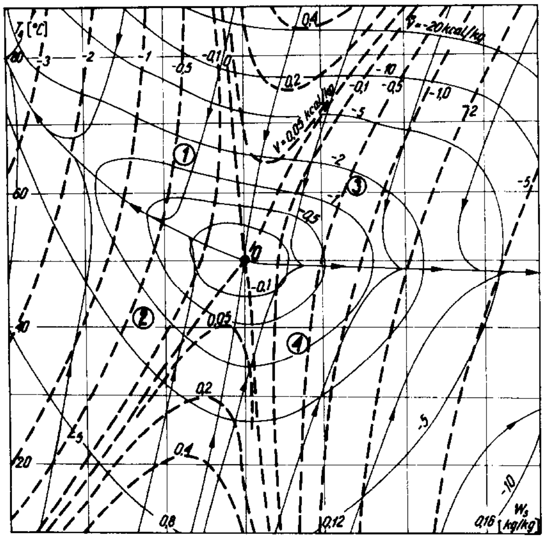

FIG. 4. Lines V = constant and $\dot{V}$ = constant, as well as trajectories for adiabatic countercurrent process, $Q = -2$, $Le = 1$.

$$V[I_s, W_s, i_m^0, X_m^0] = T^{0t}(s_m^0 - s_m). \tag{39}$$

(The results in Figs. 3 and 4 refer to a function V given by the above formula.)

In the isoentropic flow system $s_m = s_m^0$ and $X_m = X_m^0$, and inequality (33) reduces to the form:

$$\frac{\mathrm{d}}{\mathrm{d}\tau}\{I_s + Qi_g[s_g, X_g]\} \leqslant 0; \tag{40}$$

i.e.

$$\frac{\mathrm{d}}{\mathrm{d}\tau}\left\{I_s + Qi_g\left[\frac{s_m^0 - S_s[I_s, W_s]}{Q}, \frac{X_m - W_s}{Q}\right]\right\} \leqslant 0. \tag{41}$$

Thus, the Liapunov function is mean gas-suspension enthalpy in excess of its mean enthalpy in the singular state which is expressed in terms of the invariants s_m^0, X_m^0 and state variables

$$V[I_s, W_s, s_m^0, X_m^0] = i_m[s_m^0, X_m^0, I_s, W_s] - i_m[s_m^0, X_m^0, I_s^0, W_s^0]. \quad (42)$$

For a process with an isothermal gas phase, $T_g = T^0$ and $X_m = X_m^0$, inequality (33) is of the form:

$$\frac{\mathrm{d}}{\mathrm{d}\tau}\left\{I_s + Qi_g\left[T^0, \frac{X_m^0 - W_s}{Q}\right] - T^0\left(S_s[I_s, W_s] + Qs_g\left[T^0, \frac{X_m^0 - W_s}{Q}\right]\right)\right\} \leqslant 0. \quad (43)$$

Designating

$$g_m[T^0, X_m^0, I_s, W_s] \equiv i_m - T^0 s_m \quad (44)$$

using equation (43), a conclusion is made that the Liapunov function is

$$V[T_0, X_m^0, I_s, W_s] = g_m[T^0, X_m^0, I_s, W_s] - g_m[T^0, X_m^0, I_s^0, W_s^0]. \quad (45)$$

Note, that if both phases have a temperature, T^0, then the function g_m defined by formula (45) is a mean thermodynamic potential of a two-phase jet.

For a process with constant gas-phase parameters, $T_g = T^0$, $\mu_{\omega g} = \mu_\omega^0$. So in inequality (33) the gas-phase parameters vanish and only solid and equilibrium ones remain:

$$\frac{\mathrm{d}}{\mathrm{d}\tau}\{I_s - T^0 S_s[I_s, W_s] - \mu_\omega^0 W_s\} \leqslant 0. \quad (46)$$

Designating

$$\Gamma[I_s, W_s, T^0, \mu_\omega^0] = I_s - T^0 S_s[I_s, W_s] - \mu_\omega^0 W_s \quad (47)$$

gives the Liapunov function in the form:

$$V[T^0, \mu_\omega^0, I_s, W_s] = \Gamma[I_s, W_s, T^0, \mu_\omega^0] - \Gamma[I_s^0, W_s^0, T^0, \mu_\omega^0]. \quad (48)$$

6.3. *Time derivatives of the Liapunov functions*

A comparison of (33)–(35) and (39) shows that for the adiabatic case a time derivative of function (39) follows from formula (36), in which a temperature, T_g, before a square bracket should be replaced by an environment temperature T^{0t}. Substitution of the right-hand sides of (20) and (21) with $i_m = i_m^0$, $X_m = X_m^0$ into modified formula (36), as is done above, yields a derivative of function (39) adjoint with a set of equations (20) and (21):

$$\dot{V}[I_s, W_s, i_m^0, X_m^0] = T^{0t}\left\{\left(\frac{1}{T_g[I_s, W_s, i_m^0, X_m^0]} - \frac{1}{T_s[I_s, W_s]}\right)\left[\frac{i_m^0 - I_s}{Q} - i_s[I_s, W_s]\right) + (Le - 1)i_{ps}[I_s, W_s]\left(\frac{X_m^0 - W_s}{Q} - X_s[I_s, W_s]\right)\right] + \left(\frac{\mu_{\omega s}[I_s, W_s]}{T_s[I_s, W_s]} - \frac{\mu_{\omega g}[I_s, W_s, i_m^0, X_m^0]}{T_g[I_s, W_s, i_m^0, X_m^0]}\right) \times \left(\frac{\dot{X}_m - W_s}{Q} - X_s[I_s, W_s]\right)\right\}, \quad (49)$$

where

$$T_g[I_s, W_s, i_m^0, X_m^0] = T_g\left[\frac{i_m^0 - I_s}{Q}, \frac{X_m^0 - W_s}{Q}\right] \quad (50)$$

$$\mu_{\omega g}[I_s, W_s, i_m^0, X_m^0] = \mu_{\omega g}\left[\frac{i_m^0 - I_s}{Q}, \frac{X_m^0 - W_s}{Q}\right]. \quad (51)$$

Similarly, for a system with an isothermal gas phase we have:

$$\dot{V}[I_s, W_s, T^0, X_m^0] = T^0\left\{\left(\frac{1}{T^0} - \frac{1}{T_s[I_s, W_s]}\right) \times \left(i_g\left[T^0, \frac{X_m^0 - W_s}{Q}\right] - i_s[I_s, W_s] + (Le - 1)i_{ps}[I_s, W_s]\left(\frac{X_m^0 - W_s}{Q} - X_s[I_s, W_s]\right)\right) + \left(\frac{\mu_{\omega s}[I_s, W_s]}{T_s[I_s, W_s]} + \frac{\mu_{\omega g}[T^0, X_m^0, I_s, W_s]}{T_0}\right) \times \left(\frac{X_m^0 - W_s}{Q} - X_s[I_s, W_s]\right)\right\}. \quad (52)$$

It is for a reader to derive the appropriate formulae for other processes.

The functions $\dot{V}$ are described by equations (49) and (52), and the similar functions for another cases should satisfy the inequality:

$$\dot{V} \leqslant 0 \quad (53)$$

which follows from the second thermodynamics law.*

Since for a real system inequality (53) is always valid, then based on the Liapunov theorem, the real trajectories of a process are stable when the function V is

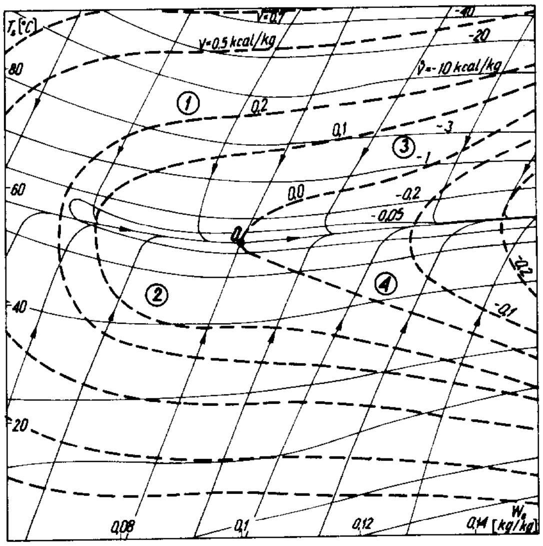

FIG. 5. Lines, V = constant and $\dot{V}$ = constant, as well as trajectories for adiabatic countercurrent flow process with isothermal gas phase, $Q = -2$, $Le = 1$.

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*For the states I_s, W_s, in which inequality (53) is not satisfied, the model for a process gives the results inconsistent with the reality. Based on equations (49), (52) and the similar ones, calculation serves only for finding regions essential (qualitative) inconsistency of the system and its model. Such check is usually advisable, because the kinetic equations are not probably universal over a wide range of states.

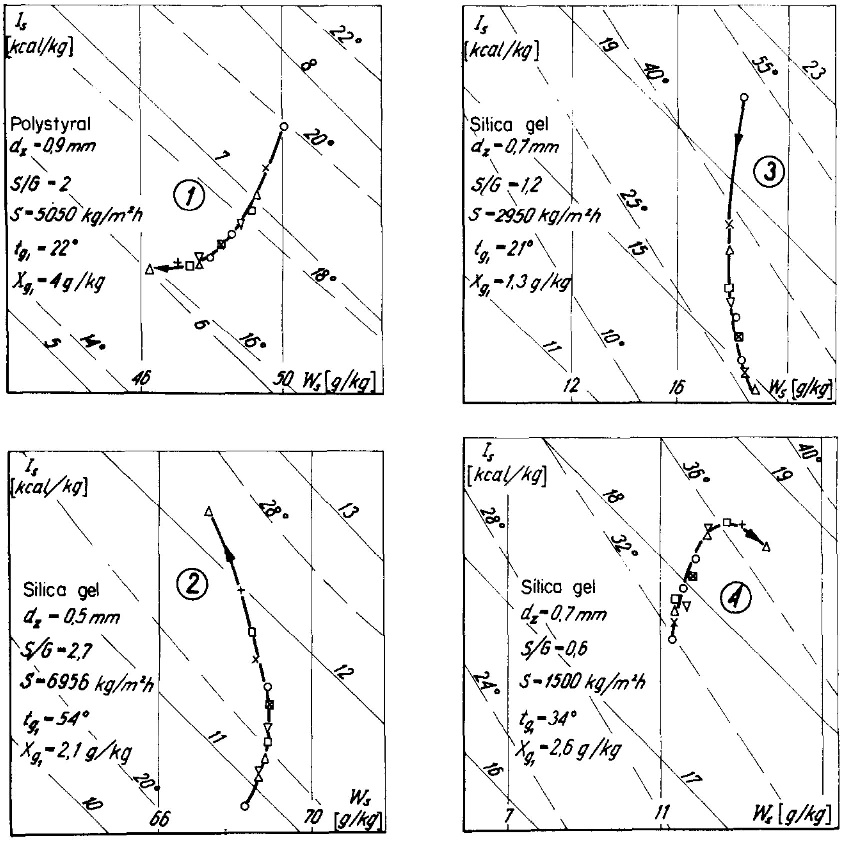

FIG. 6. Test trajectories of polystyrol and silica gel for countercurrent flow drying and moistening.

positively defined with respect to variables I_s, W_s. Moreover, if in any small vicinity of a singular point there exists a domain, in which the function V is negative, then the trajectories are unstable on the basis of Chetaev's theorem.

The appropriate numerical results for the processes studied are discussed in Section 7.

7. NUMERICAL RESULTS AND CONCLUSIONS

Calculations are made of a silica gel–water–air system. It is assumed that $I_s^0 = 7.6\,\text{kcal}\,\text{kg}^{-1}$, $W_s^0 = 0.1\,\text{kg}\,\text{kg}^{-1}$, then $T_s^0 = 50\,^\circ\text{C}$.

The results for functions V and $\dot{V}$ and for trajectories (found numerically) are plotted on the T_s–W_s diagram (Figs. 3–5).

On all the diagrams, the lines $V = \text{constant}$ are closed curves for negative functions. This witnesses that the kinetic equations analyzed satisfy necessary conditions of the model validity. A sufficient condition [7] is a good agreement between a model and real behaviour of a system.

For all concurrent flow processes studied, the shape of a curve for the Liapunov function $V[I_s, W_s]$ is qualitatively close to that for a sphere segment, whose minimum lies at a singular point (Fig. 3). Positive definiteness V, negative definiteness $\dot{V}$ and tending of the function V to zero together with a vector norm ($T_s - T_s^0$, $W_s - W_s^0$) prove asymptotic stability of the trajectories of flow processes discussed.

The same conclusion may be made regarding a process with constant gas parameters.

For constant gas parameters and when $Le = 1$, a set of equations (12) and (13) describes equilibrium cross-current flow in a horizontal fluidized bed [5]. Thus, the trajectories of this process are also asymptotically stable.

A large qualitative nonuniformity of the Liapunov function appears in countercurrent flows. In an adiabatic process (Fig. 4) the surface $V[I_s, W_s]$ is shaped as a saddle, whose stationary point is a singular point of the trajectories. Domains of negative values of V appear which prove the instability of a pseudo-equilibrium state. Trajectories, originating in the domain where $V > 0$, first tend to a singular point, then depart from it to the domain where $V < 0$. Two specific solutions approach a singular point at $\tau \to +\infty$, and those for $\tau \to -\infty$ are the lines called separatrices. These lines divide a state plane into four regions, each possessing the same properties of trajectories (path, extrema of temperature or moisture content etc.). Knowledge of invariants of the trajectory analyzed allows determination of a singular point, Liapunov function and hence separatrix path. This results in finding a qualitative nature of trajectories as curves leading always in the direction of the decreasing potential V. This fact is important in case of unreliability or unavailability of kinetic data.

The case of isentropic trajectories of a countercur-

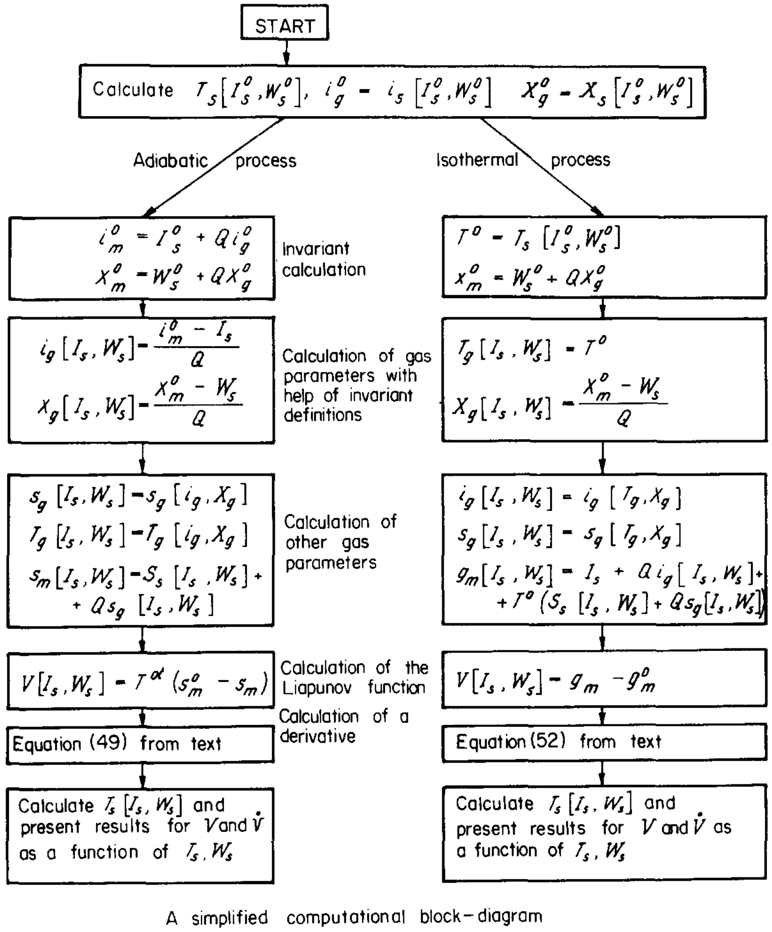

FIG. 7. Simplified block-diagram of calculations.

rent process appears to be qualitatively identical to the adiabatic one.

A comparatively seldom type of instability appears in a process with a uniform gas-phase temperature $T_g = T^0$ (Fig. 5). The course of a line V = constant shows that the Liapunov function is consistent with a surface, which at a singular point has a minimum (with respect to a variable, T_s) and also an inflection (with respect to a variable, W_s). Owing to the fact that trajectories may be only in the direction of a decreasing potential, V, it follows with regard to the shape of the line V = constant in Fig. 5 that in the process under consideration there should, very frequently, appear trajectories with moisture content increasing with time (solid moistening). The course of the predicted trajectories in Fig. 5 confirms this conclusion. In this case the unstable singular point is called a nodal-saddle point.

The study of the Liapunov function allows us to avoid design errors which appear due to intuitive prescription of initial process states. This leads to systematization of predicted (Figs. 3–5) and experimental (Fig. 6) trajectories.

The results in Fig. 6 refer to the trajectories of countercurrent drying of granulated silica gel and polystyrol in the adiabatic column 87 mm dia., cf. [7].

Four typical curves in Fig. 6 were predicted theoretically by a qualitative analysis of the function V (Fig. 4). Their location differs in frame of separatrices which represent a natural coordinate system of a process. A pure thermodynamic criterion of separatrices allows comparison of curves for different materials and at different singular points.

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APPROCHE THERMODYNAMIQUE DES PROPRIETES QUALITATIVES DES TRAJECTOIRES DU TRANSFERT DE CHALEUR ET DE MASSE DANS DES SYSTEMES GAZ-SOLIDE.

I—SYSTEMES CHIMIQUEMENT INERTES

Résumé—On étudie les propriétés qualitatives et la stabilité des trajectoires des transferts de chaleur et de masse dans des écoulements gaz-solide.

On construit des fonctions de Liapunov basées sur le principe thermodynamique et l'on montre que l'instabilité des trajectoires des processus à contre-courant est thermodynamiquement fondée. On porte attention sur le caractère général de l'approche thermodynamique de la stabilité et des propriétés qualitatives des trajectoires.

THERMODYNAMISCHE BEHANDLUNG DER QUALITATIVEN EIGENSCHAFTEN VON TRAJEKTORIEN BEI WÄRME- UND STOFFÜBERTRAGUNG IN GAS-FESTSTOFF-SYSTEMEN

I NICHT-REAGIERENDE SYSTEME

Zusammenfassung—Es werden qualitative Eigenschaften und die Stabilität von Trajektorien bei simultanen Wärme- und Stoffübertragungsprozessen in Gas-Feststoff-Systemen studiert. Nach thermodynamischen Grundlagen werden Liapunov-Funktionen aufgestellt, und die Instabilität der Trajektorien für Gegenstrom-Systeme wird thermodynamisch begründet. Betont wird der allgemeine Charakter der thermodynamischen Behandlung von Stabilität und qualitativen Eigenschaften der Trajektorien.

ТЕРМОДИНАМИЧЕСКИЕ МЕТОДЫ ИССЛЕДОВАНИЯ КАЧЕСТВЕННЫХ СВОЙСТВ ТРАЕКТОРИИ ПРОЦЕССОВ ТЕПЛО- И МАССООБМЕНА В ПРОТОЧНЫХ СИСТЕМАХ ГАЗ — ТВЕРДОЕ ТЕЛО — I. СИСТЕМЫ БЕЗ ХИМИЧЕСКОЙ РЕАКЦИИ

Аннотация — Исследуются качественные свойства и устойчивость траекторий, установившихся в ходе проточных процессов между газом и твердым телом, в которых происходят одновременно массо- и теплопередача.

На термодинамической основе построены функции Ляпунова. Термодинамически обоснована неустойчивость траекторий противоточных процессов.

Подчеркивается общий характер изложенного термодинамического подхода к исследованию устойчивости и качественных свойств траектории.