The dependence of the residual value of the functional on the number of terms in the equation is shown in Fig. 1. Analysis of this graph shows that with minimization of the relative deviations of the velocity, the decrease in residual value of the error is increased, i.e., with the given value of the total error, the equation will contain a smaller number of terms.

On the basis of the foregoing, it may be concluded that the proposed method allows: improvement in the description of the total mass of P, v, T data as a whole; improvement in the reproducibility of the P, v, T surface in the vicinity of the triple point and the saturation curve; and reduction in the number of terms in the equation of state with a specified level of error.

NOTATION

w_i, weight of the i-th experimental point; $\overline{Y}$, dependent-variable vector; X, matrix of the dependent-variable values; ε, absolute-deviation vector; $\overline{\delta}$, relative-deviation vector; Y_i, value of the dependent variable at point i; x_{qk}, value of the q-th independent variable at point k; z, compressibility; ρ, density; $\omega = \rho/\rho_{cr}$, reduced density; $\theta = T_{cr}/T$, reduced temperature; T, temperature; T_{cr}, critical temperature; $b_{ij}, c_{ij}, d_{ij}, e_{ij}-$, parameters of the equation of state; h, enthalpy; c_v, isochoric specific heat; $\overline{b}$, vector of unknown coefficients of the equation; N, number of experimental points; M, number of coefficients of the equation; $\overline{\varepsilon}', \overline{\delta}', V'$, transposed matrices.

LITERATURE CITED

1. V. V. Sychev et al., Thermodynamic Properties of Nitrogen [in Russian], Standartov, Moscow (1977).
2. G. A. Seber, Linear Regression Analysis, Wiley (1977).
3. Norman Draper and H. Smith, Applied Regression Analysis, Wiley (1966).
4. E. Z. Demidenko, Linear and Nonlinear Regression [in Russian], Statistika, Moscow (1981).
5. V. V. Altunin, Thermophysical Properties of Carbon Dioxide [in Russian], Standartov, Moscow (1975).
6. I. F. Golubev, V. P. Kiyashova, I. I. Perel'shtein, and E. B. Parushin, Thermophysical Properties of Ammonia [in Russian], Standartov, Moscow (1978).

GENERALIZED INTEGRAL VARIATIONAL PRINCIPLES OF PHENOMENOLOGICAL

THERMODYNAMICS OF IRREVERSIBLE PROCESSES, AND THE NATURE OF VARIATION

OF THERMODYNAMIC ACTION

I. P. Vyrodov

UDC 536.75

Generalized integral variational principles of phenomenological thermodynamics of irreversible processes (PTIP), as formulated by the present author, are stated.

1. Previous History of Integral Variational Principles. The first attempts of applying the apparatus of ordinary phenomenological thermodynamics (OPT) to dynamic systems [1] peaked in the construction of a linear formalism in Onsager's work [2]. The further development of dynamic methods of describing nonequilibrium systems [3-6] acquired global character, but Truesdell [6] provided a quite negative and nonobjective [7] estimate of the linear PTIP [2, 8]. A whole series of fundamental laws, reflecting the evolution of nonequilibrium thermodynamic systems, was established by means of the linear PTIP: the I. Prigogine minimum principle of entropy production [8], and the Onsager minimum principle of energy dissipation [2]. A generalized minimum principle of entropy production [9], following from the more general extremum integral variational principle in the entropy representation [10], was formulated for nonlinear Onsager systems.

A fruitful application of the ideas of linear PTIP is reflected in [11, 12]. However, the linear "credo" is overestimated in the formulation of PTIP variational principles in [2, 5, 13], since the choice of the dissipation potentials is essentially based on the linear PTIP formalism. Besides, these principles, being the basic principles of field theory in thermodynamics [5], are in contradiction with the requirement of their invariance with respect to Poincaré—Lorentz transformations. This unjustified heuristic approach, reducing in later work to conclusions from the formulated variational principles of differential equations of transport and hydrodynamics, cannot serve as the reason of stating general variational PTIP problems, since it cuts off the path to disclosing the nature of PTIP problems and to constructing its axiomatics, subsequently based on OPT ideas. These problems were elaborated in [9, 10, 14-27], completing the formulation of ordinary [16-19, 27, 28] and generalized [20, 21] PTIP variational principles.

2. Physical Essence of Axiomatically Closed PTIP, and Ideas of Constructing Integral Variational Principles of Continuous PTIP. The description of an arbitrary nonequilibrium dynamic system by the apparatus and formalism of OPT is possible if it is assumed that the thermodynamic parameters of the dynamic system depend on time autonomously. However, since a rigorous determination of thermodynamic parameters is given only for thermodynamically equilibrium and quasistatic states, for a nonequilibrium and irreversible continuous dynamic system at all points of space such a determination is possible only locally by means of an additional principle, the local equilibrium principle (LEP). A phenomenological approach to establishing the applicability region of LEP [21] makes it possible to determine the correlation dependence between variations of the state parameters, as well as the region of intercell dissipation. The basic laws and formalism of OPT, augmented by LEP, constitute the axiomatically closed nature of PTIP. Consequently, the extremum principles of PTIP, reflecting the evolution of a dynamic system, are contained in the closed system of PTIP axioms. Indeed, let the thermodynamic potential $z(\eta)$ be a local quantity of the continuous thermodynamic system. The additive nature of this quantity makes it possible to pass from local extreme principles to an integral path of varying the thermodynamic action ΔZ, obtained by means of the substantial derivative

$$\overset{\circ}{\delta} \int_{V} \int_{t_1}^{t_2} \rho \Delta \dot{z} dv dt = \overset{\circ}{\delta} \int_{V} \int_{t_1}^{t_2} (\sigma_z - \operatorname{div} I_z)\, dv dt = 0,$$

(1)

if the region of integration does not contain mobile boundaries.

In a relativistically invariant representation

$$\overset{\circ}{\delta} \int_{V_4} \mathscr{L}(\chi_h,\ \eta_h,\ \eta_{h|i},\ x^i)\, d^4x = 0,$$

(2)

where χ_k is the set of nonvarying thermodynamic functions, and the variation operator $\overset{\circ}{\delta}$ is so far defined only in the thermodynamic sense.

In the case of satisfaction of strong conservation equations, determined by the variation conditions of the thermodynamic field functions η on the boundaries of the integration region (V_4), the following Lagrange—Euler PTIP equations are valid.

$$\frac{\overset{\circ}{\delta}\mathscr{L}}{\overset{\circ}{\delta}\eta_\lambda} = \left(\frac{\partial\mathscr{L}}{\partial\eta_{\lambda|\alpha}}\right)_{,\alpha} - \frac{\partial\mathscr{L}}{\partial\eta_\lambda} = 0,$$

(3)

as well as the Hamilton equation.

Thus, in a closed system of PTIP axioms the integral variational principles are already well founded, though in themselves deprived of heuristic origin.

3. Generalized Integral Variational Principles, and Nature of Variation. Taking into account the integral variational principle (1) and the representation for the generalized thermodynamic potentials

$$z_{h_1} = \psi_h = u - \sum_{(i)}^{h} \eta^i \eta_i,\quad z_{h_2} = \Phi_h = s - \sum_{(i)}^{h} \eta^{*i} \eta_i,$$

(4)

we write the generalized integral variational principles in the energy and entropy representations:

$$\overset{\circ}{\delta} \int_{V_4} \rho \Delta \dot{\psi}_h d^4x = 0, \quad \begin{array}{l} \eta^j = \text{const} \quad (j = 1, 2, \ldots, k), \\ \eta_j = \text{const} \quad (j = k+1, \ldots, r), \end{array} \tag{5}$$

$$\overset{\circ}{\delta} \int_{V_4} \rho \Delta \dot{\Phi}_h d^4x = 0, \quad \begin{array}{l} \eta^{*j} = \text{const} \quad (j = 1, 2, \ldots, k), \\ \eta_j = \text{const} \quad (j = k+1, \ldots, r). \end{array} \tag{6}$$

A variational principle follows from (5) at k = 2 for the Gibbs free energy

$$\overset{\circ}{\delta} \int_{V_4} \rho \Delta \dot{g} d^4x = 0, \quad T, \; p; \; n_1, \; n_2, \; \ldots, \; n_m = \text{const.} \tag{7}$$

A variational principle follows from (5) at k = 1 for the Helmholtz free energy

$$\overset{\circ}{\delta} \int_{V_4} \rho \Delta \dot{f} d^4x = 0, \quad T, \; V; \; n_1, \; n_2, \; \ldots, \; n_m = \text{const.} \tag{8}$$

A variational principle in the energy representation follows from (5) at k = 0 (the Onsager principle of minimum energy dissipation)

$$\overset{\circ}{\delta} \int_{V_4} \rho \Delta \dot{u} d^4x = 0, \quad s, \; V; \; n_1, \; n_2, \; \ldots, \; n_m = \text{const.} \tag{9}$$

A variational principle in the entropy representation follows from (6) at k = 0, generalizing the Prigogine principle of minimum entropy production,

$$\overset{\circ}{\delta} \int_{V_4} \rho \Delta \dot{s} d^4x = 0, \quad u, \; V; \; n_1, \; n_2, \; \ldots, \; n_m = \text{const.} \tag{10}$$

The variational principles (7)-(10) contain definite information on the nature of variation of thermodynamic parameters (continuous field functions), appearing in the thermodynamic Lagrangians. Naturally, certain restrictions are also imposed on the generalized thermodynamic forces and flows, since the latter can depend on the nonvarying parameters [20]. Taking into account the density of thermodynamic second-order Lagrangian in the n-dimensional space, one obtains the expression

$$(\mathscr{L} - \Pi^{\lambda j}\eta_{\lambda,j}) \Delta x_j + \Pi^{\lambda j}\Delta\eta_\lambda = 0, \tag{11}$$

valid on the surface (V_4) [21]. In this expression we have variations of two types, realized in continuous variations of the following four cases: 1) $\Delta\eta_\lambda = 0$, $\Delta x_j = 0$; 2) $\Delta\eta_\lambda = 0$, $\Delta x_j \neq 0$; 3) $\Delta\eta_\lambda \neq 0$, $\Delta x_j = 0$; 4) $\Delta\eta_\lambda \neq 0$, $\Delta x_j \neq 0$. The first case corresponds to functional variation; therefore the following variational principle is valid:

$$\delta \int_{V_4} (\sigma - \mathscr{H}) d^4x = 0. \tag{12}$$

In the second case the density of thermodynamic Hamiltonian is

$$\mathscr{H} = \Pi^{\lambda j}\eta_{\lambda,j} - \mathscr{L} = 0, \tag{13}$$

and this implies [16, 17] that

$$\text{div} \, I_s = \mathscr{H} = 0, \quad \mathscr{L} = \sigma = \Pi^{\lambda j}\eta_{\lambda,j}; \tag{14}$$

therefore, the minimum principle of entropy production is satisfied

$$\Delta \int_{V_4} \sigma d^4x = 0. \tag{15}$$

In the third case:

$$\Pi^{\lambda j} = 0, \quad \mathscr{L} = \mathscr{H}, \tag{16}$$

and we reach the minimum principle of dissipation of a Hamilton system

$$\delta \int_{V_4} \mathscr{H} d^4x = 0.$$
(17)

In the fourth case relationship (11) can be satisfied under the condition

$$\mathscr{L} = \Pi^{\lambda j} \eta_{\lambda,j} - \Pi^{\lambda j} \frac{\Delta \eta_\lambda}{\Delta x_j} = \sigma - \mathscr{H};$$
(18)

therefore the following variational principle is valid:

$$\Delta \int_{V_4} (\sigma - \mathscr{H}) d^4x = 0.$$
(19)

The variation principles (15) and (17) obtained by us are the generalization of the Prigogine minimum entropy production principle and the Onsager minimum energy dissipation principle, respectively, formulated by them for a restricted class of thermodynamic systems. The variational principles (12) and (19) have a more general character. Since, without loss of generality, (19) can contain variations of four types: total, functional, substantial, and local, there is no restriction on the transverse components, as imposed on the density of thermodynamic Lagrangian in the sense of restricted OPT. The principle (19) is realized when essentially dynamic conservation laws are satisfied.

4. Derivation of Partial Extremum Principles, and Criteria of Establishing Integral Variational PTIP Principles. Consider the structure of the variational principle (1). For this we write down

$$\overset{\circ}{\delta} \int_{V_4} \rho \Delta z dV dt = \overset{\circ}{\delta} \int_{t_1}^{t_2} P_z dt - \overset{\circ}{\delta} \int_{(V)} \int_{t_1}^{t_2} (I_z dF) dt = 0.$$
(20)

Let the integral production P_z and the flow I_z depend on the set of thermodynamic quantities of two types, I and X. For immobile boundaries of integration regions we have then

$$\int_{t_1}^{t_2} \overset{\circ}{\delta} P_z dt - \int_{(V)} \int_{t_1}^{t_2} \overset{\circ}{\delta} (I_z dF) = \int_{t_1}^{t_2} (\overset{\circ}{\delta}_x P_z + \overset{\circ}{\delta}_I P_z) dt - \int_{(V)} \int_{t_1}^{t_2} (\overset{\circ}{\delta} I_z dF) dt = 0$$
(21)

or

$$\overset{\circ}{\delta}_x P_z + \overset{\circ}{\delta}_I P_z - \int_{(V)} (\overset{\circ}{\delta} I_z dF) = 0.$$
(22)

This relationship connects two evolution criteria for a known flow variation $\overset{\circ}{\delta} I_z$ in terms of the surface (V). Under the condition

$$\overset{\circ}{\delta}_I P_z - \int_{(V)} (\overset{\circ}{\delta} I_z dF) \geqslant 0$$
(23)

follows from (22) the Glansdorff–Prigogine evolution criterion for P_s without restricting the generality of the dynamic equations of the nonequilibrium thermodynamic system. The variational equality (22) also contains other evolution criteria, determined by the boundary conditions for the thermodynamic system. For example, related to the inequality

$$\int_{(V_4)} (\overset{\circ}{\delta} I_z dF) \geqslant 0$$
(24)

the following equation is satisfied:

$$\overset{\circ}{\delta}_x P_z + \overset{\circ}{\delta}_I P_z \geqslant 0.$$
(25)

In the case of the linear formalism, this evolution criterion for P_s contains in it the Glansdorff–Prigogine evolution criterion for nonvirtual variations, since in this case

$$\overset{\circ}{\delta}_x P_s = \overset{\circ}{\delta}_I P_s = \frac{1}{2}\overset{\circ}{\delta}P_s. \tag{26}$$

We now show that if an arbitrary dynamic system tends to local equilibrium, then its path to this state is an extremum. Indeed, let a local equilibrium state not be satisfied in the given nonequilibrium system at moment t, but let this state be achieved at t' > t. We substitute into the correspondence t' = t + Δi the quantity $\Delta t = \tau_r(t)$, and assume that $\tau_r(t)$, being a relaxation time, is an asynchronous variation. Then, introducing the curves (el) and (nl), corresponding to the thermodynamic local equilibrium $(z)^0$ and local nonequilibrium parameters F_z, accompanied by a z-potential in the sense that $F_z \to z$, we write, with account of the properties of asynchronous variations

$$\overset{\circ}{\delta} \int_{V'} \int_{t_1}^{t_2'} (\rho\Delta\dot{z})^0 dVdt' = \overset{\circ}{\delta} \int_{V'} \int_{t_1}^{t_2'} \{\Delta\dot{f} + [(\rho\Delta\dot{z})]\tilde{\Delta}t\} dVdt' = 0, \tag{27}$$

whence

$$\overset{\circ}{\delta} \int_{V'} \int_{t_1'}^{t_2'} \{[\rho\Delta\dot{z}^0 - \Delta\dot{f}] - [\rho\Delta\dot{z}^0]\tilde{\Delta}t\} dVdt' = 0. \tag{28}$$

We analyze this relation. Assuming that

$$\overset{\circ}{\delta}[\rho\Delta\dot{z}^0(t')]\tilde{\Delta}t = 0, \tag{29}$$

the extremum principle is then satisfied for the approach rate of an arbitrary local dynamic quantity to its local equilibrium state at any moment of time t, and under the integral in (28) one can transform from primed t to nonprimed ones:

$$\overset{\circ}{\delta} \int_{V} \int_{t_1}^{t_2} [\rho\Delta\dot{z}^0(t) - \Delta F(t)] dVdt = 0. \tag{30}$$

Condition (29) implies constant accelerations, the second time derivatives of thermodynamic extensive quantities.

Thus, if the local nonequilibrium dynamic system, described by the F_z parameter, tends to a local equilibrium state at all parts of the system, then its path is extremal with respect to equal-acceleration "moving" local equilibrium $\rho\Delta z^0$-states. If this condition is not satisfied, then, transforming the integrand expression, we reach an extremum principle for the approach velocity of the dynamic system to a local equilibrium state with a displaced relaxation time

$$\overset{\circ}{\delta} \int_{V'} \int_{t_1'}^{t_2'} [\rho\Delta\dot{z}^0(t' - \tilde{\Delta}t) - \Delta F(t')] dVdt' = 0. \tag{31}$$

The principles (28), (30) reflect the extremum character of the velocity of transition of a local nonequilibrium (fluctuating) system to its local equilibrium state. This conclusion has indirect confirmation in the situation of chemical reactions, treated in [29] from the point of view of the theory transition states. The results obtained in that work can be considered as a consequence of principles (28), (30) as applied to chemical reactions, since these principles extend to arbitrary nonequilibrium dynamic systems, tending to a local equilibrium state.

As an example, consider the variational principle in the entropy form:

$$\delta\left[\int_{V}\int_{t_1}^{t_2}\sigma dVdt - \int_{(V)}\int_{t_1}^{t_2}(I_s dF) dt\right] = 0; \quad u, \ V; \ n_1, \ n_2, \ \ldots, \ n_m = \text{const.} \tag{32}$$

103

If the entropy flow I_s is not varied on the immobile surface (V), then the following generalized differential principle of minimum entropy production is valid at all points M of the system volume V

$$\delta\sigma = \delta\Sigma I_i X_i = 0$$

(33)

under the most general condition

$$(I_s)_{(V)} = \left(\frac{I_q' + \Sigma s_h I_h T}{T}\right)_{(V)} = \text{const}$$

(34)

independently of the selected formalism in the constituting equations (linear or nonlinear [9]), while the variation is carried out over X and I. Thus, separating in (34) N—n vanishing flows and n flows I_i^V, represented in terms of constant thermodynamic forces X_k, we obtain the realization condition of principle (33) upon contracting the volume V to the point M: (V)→M

$$\sum_{(v)}\left(\sum_{i=1}^{n} I_i^{(v)}(X_h)\right) = \text{const.}$$

(34')

Thus, from principle (10) we obtain both the special case of the minimum principle for entropy production for linear systems due to Prigogine, and the minimum principle of entropy production by the present author for nonlinear Onsager systems [8, 9, 17].

5. Two-Parameter Essence Density of Thermodynamic Lagrangian, and Extremum Regression of Local Equilibrium States. The use of only local equilibrium thermodynamic parameters in the density of the thermodynamic Lagrangian according to the OPT "credo," determining the potential characteristics and thermodynamic functions, makes it possible to describe only nonequilibrium dissipationless processes. In OPT, however, particularly in the Gibbs equations, no account is taken of the fluctuations of parameters from their local equilibrium values. Taking into account that the thermodynamic description of a dynamic system is valid within the limits of thermodynamic parameter fluctuations, we can relate the nonvarying parameters either to a local equilibrium state, and the varying parameters to a local nonequilibrium, in analogy with the situation when a local equilibrium state is a fluctuation from the original equilibrium state of the whole system, or conversely. Then, along with the extremum of the $(\rho\Delta\dot{z})^0$ state there also exist extrema of $(\rho\Delta\dot{z})$ states:

$$\overset{\circ}{\delta}\int_{V_4} \mathscr{L}^{z^0} dVdt = \overset{\circ}{\delta}\int_{V_4} (\rho\Delta\dot{z})^0 dVdt = 0,$$

(35)

$$\overset{\circ}{\delta}\int_{V_4} \mathscr{L}^{z} dVdt = \overset{\circ}{\delta}\int_{V_4} (\rho\Delta\dot{z}) dVdt = 0.$$

(36)

Since

$$\mathscr{L}^{z} = (\rho\Delta\dot{z}) = (\rho\Delta\dot{z})^0 + \Delta(\rho\Delta\dot{z}) = \mathscr{L}^{z^0} + \mathscr{L}^{zz^0},$$

(37)

the densities of thermodynamic Lagrangians in (35) and (36) are mutually related. The corresponding thermodynamic systems were correspondingly named by us mutually conjugate [30]. The nature of fluctuation regression of local nonequilibrium thermodynamic parameters to their local equilibrium values has the same important feature concerning the regression of fluctuations of local equilibrium parameters to their equilibrium values, namely, that the Lagrangian

$$\mathscr{L}^{zz^0} = \mathscr{L}^{z} - \mathscr{L}^{z^0}$$

includes dissipative processes due to fluctuation breakdown of local equilibrium. The extremum nature of the process, described by the integral variational principle

$$\overset{\circ}{\delta}\int \mathscr{L}^{zz^0} dVdt = 0,$$

(38)

follows from the very essence of the thermodynamic description of dynamic systems, including local nonequilibrium. The two-parameter structure $\mathscr{L}^{zz^0}$ leads to an identical description of dissipative processes by means of Lagrange—Euler equations:

$$\frac{\overset{\circ}{\delta} \mathcal{L}^{zz^0}}{\delta \eta_\lambda} = 0, \tag{39}$$

$$\frac{\overset{\circ}{\delta} \mathcal{L}^{zz^0}}{\delta \overset{c}{\eta_\lambda}} = 0, \tag{40}$$

as well as to establishing the nature of the local potential method. Each of the two equations (35) and (36) leads to the same equations of heat and mass transfer, and in this case the relation of principle (38) with local potentials is easily revealed for different physical problems. The principle (38) was also used by us for successful solution of the Benard problem [31], for calculating the width of a boundary layer in laminar film flow, in studying concentration profiles in chemical reactors and electrodialysis instruments, and other problems, carried out with co-workers in the physics department of the Krasnodar Polytechnic Institute. It has been established that in all cases the local potential method is, in all respects, inferior to the methods based on principle (38). As an example we consider the boundary layer problem.

6. Determination of Width of Dynamic Boundary Layer for Critical Laminar Film Flow.
We consider stationary laminar flow of an incompressible liquid, flowing around a planar film perpendicular to the flow. The OX axis is directed along the film, and the OY axis is directed perpendicularly to it.

The Lagrangian density of the problem is written in the form

$$\mathcal{L}^{EE^0} = \frac{1}{2} \rho \left[u_0 \left(u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} \right) - u \left(u_0 \frac{\partial u_0}{\partial x} + v_0 \frac{\partial u_0}{\partial y} \right) \right] + L_{\mu\mu} \frac{\partial u}{\partial y} \frac{\partial u_0}{\partial y} . \tag{41}$$

We take into account that near the critical point, selected as the origin for reference, the velocity and pressure distributions are determined by the equations [32]

$$u = xf'(y), \; v = -f(y), \tag{42}$$

$$p_0 - p = \frac{1}{2} \rho a^2 [x^2 + F(y)]. \tag{43}$$

Performing the affine coordinate transformation

$$\eta = \sqrt{\frac{a}{v}} \, y, \; f(y) = \sqrt{av} \varphi(\eta), \tag{44}$$

we reduce the Lagrangian to the form

$$\mathcal{L}^{EE^0} = \rho x^2 a^3 \left\{ \frac{1}{2} \left[\varphi_0'(\varphi'^2 - \varphi\varphi'') - \varphi'(\varphi_0'^2 - \varphi_0\varphi_0'') \right] + \varphi''\varphi_0'' \right\} . \tag{45}$$

Substituting the density obtained into the variational principle (38), and choosing as trial functions

$$\varphi' = 3z - 3z^2 + z^3, \; \varphi_0' = 3z_0 - 3z_0^2 + z_0^3 \tag{46}$$

($z = \eta/h$), after integration and variation we obtain for the width of the boundary layer

$$1,4881h^2 = 9, \tag{47}$$

whence we find

$$h = 2,459. \tag{48}$$

The result obtained is a good approximation to the exact value [32]

$$h = 2,4. \tag{49}$$

In the case of nonstationary flow, there appear in the Lagrangian density (41) additional time derivatives of the field functions:

$$\mathcal{L}^{EE^0} = \rho x^2 a^3 \left\{ \frac{1}{2} \left(\varphi_0' \frac{\partial \varphi'}{\partial \tau} - \varphi' \frac{\partial \varphi_0'}{\partial \tau} \right) + \frac{1}{2} \left[\varphi_0'(\varphi'^2 - \varphi\varphi'') - \varphi'(\varphi_0'^2 - \varphi_0\varphi_0'') \right] + \varphi''\varphi_0'' \right\}, \tag{50}$$

where $\tau = t/\alpha$. We substitute the trial functions (46) into the density (50), assuming that the boundary layer width h is time dependent. We integrate over x and $\bar{\eta}$, and use the Lagrange—Euler equation; then to determine the dynamics of the boundary layer we obtain the ordinary differential equation

$$0.81h^{-1}\dot{h} + 1.4881 - 9h^{-2} = 0. \tag{51}$$

The result of integration for the initial condition h = 0 at τ = 0 is

$$h = 2.459 \sqrt{1 - e^{-3.4\tau}}. \tag{52}$$

The boundary layer width at the initial stage of development can be determined from the equation

$$h = 4.5 \sqrt{\tau}. \tag{53}$$

As the next example we consider the work of a chemical reactor under isothermal conditions. We study the establishment regime, and adopt the following additional simplifying assumptions: the liquid velocity v in the reactor is parallel to the axis coordinate x, and is constant over the whole cross section. In this case the original equation for the local concentration c can be written in the form

$$v \frac{\partial c}{\partial x} = D \frac{\partial^2 c}{\partial x^2} - kc^s, \tag{54}$$

where D is the diffusion coefficient, and k and s are parameters characterizing the reaction rate. The boundary conditions are written in the form

$$\text{at} \quad x = 0, \quad c = c_1; \quad x = L, \quad \partial c/\partial x = 0, \tag{55}$$

where L is the reactor size along the x axis.

In the given example we use the symmetrized density of thermodynamic potential in the form

$$\mathscr{L} = \frac{v}{2} \left(c^0 \frac{\partial c}{\partial x} - c \frac{\partial c^0}{\partial x} \right) - D \frac{\partial c}{\partial x} \frac{\partial c^0}{\partial x} - kc^{0s}c. \tag{56}$$

It is easily seen that the Lagrange—Euler equation with the use of the thermodynamic Lagrangian density (56) reduces to Eq. (54).

We introduce one more restriction: we put s = 1. In this case one can compare the approximate solution obtained by us with the exact one. Besides, it appears possible to compare the solution with the approximate one, obtained by the local potential method.

We seek a solution in the form

$$c = c_1 \sum_{(i)}^{n} [1 + a_i f_i(x)], \tag{57}$$

$$c^0 = c_1 \sum_{(i)}^{n} [1 + a_i^0 f_i(x)], \tag{58}$$

where the functions f_i can be of arbitrary shape, but must satisfy the boundary conditions

$$f_i(0) = 0; \quad f_i'(L) = \frac{\partial f_i(L)}{\partial x} = 0. \tag{59}$$

The coefficients a_i are subject to determination from the extremum condition, having the following form in the given case:

$$\left(\frac{\partial \mathscr{L}}{\partial a_i} \right)_{a_i^0} = 0, \quad i = 1, 2, \ldots, n. \tag{60}$$

Substituting expansions (57), (58) into the variational equations (60), we obtain a system of linear algebraic equations, whose solution is not difficult. To obtain numerical

TABLE 1. Comparison of Approximation Solution of Eq. (54) by the Local Potential Method (I) and the Suggested Method, Eq. (57) (II) for Various Approximations

x	First approximation		Second approximation		Third approximation		Exact solution
	I	II	I	II	I	II	
0,1	0,9823	0,8242	0,8670	0,7433	0,7649	0,7643	0,7642
0,3	0,9526	0,5282	0,6379	0,4030	0,4469	0,4475	0,4478
0,5	0,9303	0,3062	0,4300	0,2411	0,2665	0,2664	0,2664
0,75	0,9128	0,1328	0,2486	0,1950	0,1520	0,1514	0,1511
1,0	0,9070	0,075	0,1928	0,2062	0,1150	0,1157	0,1159

results we assign the physical parameters on which the constants a_i depend. Let $k = 1.0$ sec^{-1}, $D = 0.1$ m^2/sec, $V = 0.1$ m/sec, $L = 1$ m. In principle, one can substitute the coefficients k, D, V, and L into the equations, and, calculating the corresponding determinant, find the dependence of a_1, a_2, a_3 on the physical parameters characterizing processes in the system. This is one of the advantages of the approximate methods. However, we do not explore this purpose here. To compare the approximate results with the exact solution, we calculate the coefficients a_1, a_2, a_3.

We use Eqs. (57), (58) to find the approximate solution (Table 1). It is seen from the table that the third approximation is required to obtain good agreement between the exact and approximate solution. If the trial functions were chosen not as polynomials, but as the exact solution, of exponential nature, we could confine ourselves to a lower order approximation.

Comparison with the approximate solution, obtained by the local potential method, makes it possible to draw the following conclusions. Obviously, the suggested method has better convergence properties in the present case. Thus, the mean relative error in the second approximation is in the present case 25%, while the local potential method gives 50%. In the third approximation both methods provide an adequate solution, but the solution obtained by the suggested method is in better agreement with the exact solution.

NOTATION

$\overset{o}{\delta}$, operator of thermodynamic variation; ρ, mass density; σ_z, local derivative of the parameter z; V_4, four-dimensional volume; $\mathscr{L}$, Lagrangian density; n_k, $n_{k/i}$, thermodynamic functions and their derivatives with respect to four coordinates, respectively; η^i, η_i, intensive and extensive thermodynamic parameters; $\mathscr{H}$, Hamiltonian density; $II^\lambda j$, tensor of generalized thermodynamic 4-momenta; I_z, flow of the parameter z; dF, element of the surface comprising the system; $(\dot{\ldots}) = \dfrac{d(\ldots)}{dt}$, total derivative with respect to time; X_i, thermodynamic force; P_z, integral product of the parameter z.

LITERATURE CITED

1. W. Thomson (Lord Kelvin), "Application of thermodynamics to dynamic systems," Proc. R. Soc. Edinburgh, No. 3, 225–240 (1854).
2. L. Onsager, "Reciprocal relations in irreversible processes," Phys. Rev., 37, 405–425; 38, 2265–2285 (1931).
3. J. J. Thomson, Applications of Dynamics in Physics in Physics and Chemistry [in German], Leipzig (1890).
4. S. A. Boguslavskii, Selected Works in Physics [in Russian], Nauka, Moscow (1961).
5. I. Dyarmati, Non-Equilibrium Thermodynamics: Field Theory and Variational Principles, Springer-Verlag (1970).
6. C. A. Truesdell, Six Lectures on Modern Natural Philosophy, Springer-Verlag (1966).
7. I. P. Vyrodov, in: Studies in Thermal Conduction and Radiative Heat Transfer Processes in Condensed Media [in Russian], Tr. Krasnodar. Politekh. Inst., No. 51, Krasnodar (1973), pp. 5–46.
8. I. Prigogine, Introduction to Thermodynamics of Irreversible Processes, Interscience, New York (1968).
9. I. P. Vyrodov, "The principle of minimum entropy production for linear and nonlinear systems," Zh. Fiz. Khim., No. 6, 1601–1602 (1980).
10. I. P. Vyrodov, "Asymptotic phenomenological thermodynamics of irreversible processes and evolution criteria of thermodynamic systems," VINITI, No. 2127-78.

11. P. Glansdorff and I. Prigogine, Thermodynamic Theory of Structure, Stability, and Fluctuations, Wiley-Interscience (1971).

12. G. Nicolis and I. Prigogine, Self-Organization in Nonequilibrium Systems, Wiley (1977).

13. G. Vojta, "Hamilton's formalism in thermodynamic theory of irreversible processes of continuous systems," Acta Chim. Hung., 54, 55-63 (1967).

14. I. P. Vyrodov, in: All-Union Conference on Thermodynamic Irreversible Processes and Applications, Chernovtsy (1972), pp. 37-41.

15. I. P. Vyrodov, in: Thermodynamics and Kinetics of Biological Processes [in Russian], Nauka, Moscow (1980), pp. 205-214.

16. I. P. Vyrodov, "Basic variational principles of thermodynamic irreversible processes, and the construction of its formalism," VINITI, No. 3982-77.

17. I. P. Vyrodov, "Variational principles of phenomenological thermodynamics of irreversible processes," in: All-Union Conference Kinetics and Thermodynamics of Transient Processes in Biological Systems, September 12-14, 1977 (Moscow).

18. I. P. Vyrodov, in: Mechanics of Elastometers [in Russian], Krasnodar (1978), pp. 47-51.

19. I. P. Vyrodov, in: Problems in Phase Transition Physics [in Russian], Kalinin State Univ., Kalinin (1978), pp. 3-10.

20. I. P. Vyrodov, "Generalized variational principles of continuous phenomenological thermodynamics of irreversible processes," VINITI, No. 1791-79.

21. I. P. Vyrodov, in: Thermodynamics of Irreversible Processes and Mathematical Modeling of Transport Phenomena [in Russian], Krasnodar (1979), pp. 4-6.

22. I. P. Vyrodov and A. V. Lavrent'ev, "Correct variation in the basic variational principle of thermodynamics of irreversible processes, and derivation of basic transport equations," in: Thermodynamics of Irreversible Processes and Mathematical Modeling of Transport Phenomena [in Russian], Krasnodar (1979), pp. 6-7.

23. I. P. Vyrodov and A. I. Gavrilov, "The essence of the local equilibrium principle for the Gibbs equation, including dissipative functions," in: Thermodynamics of Irreversible Processes and Mathematical Modeling of Transport Phenomena [in Russian], Krasnodar (1979), pp. 7-8.

24. I. P. Vyrodov, A. V. Lavrent'ev, and A. I. Gavrilov, "Variational principles of thermodynamics of irreversible processes, and related systems," VINITI, No. 2798-79.

25. I. P. Vyrodov and A. I. Gavrilov, "Derivation of transport equations from the entropy formulation of the variational principles," VINITI, No. 2808-79.

26. I. P. Vyrodov, in: Problems in Phase Transition Physics [in Russian], Kalinin State Univ., Kalinin (1979), pp. 67-80.

27. A. V. Lavernt'ev and I. G. Khreshik, "Generalized principle of the Vyrodov minimum entropy production principle, and derivation of transport equations from the variational principle of thermodynamics of irreversible processes," VINITI, No. 2128-78.

28. I. P. Vyrodov, A. V. Lavrent'ev, and A. I. Gavrilov, in: 7th Int. Congress of Cement Chemistry [in French], II-29, Paris (1980), pp. 17-26.

29. M. I. Shakhparonov, "Possible formulation of a new principle of nonequilibrium thermodynamics, and several consequences," Zh. Fiz. Khim., No. 12, 3043-3047 (1979).

30. I. P. Vyrodov and A. I. Gavrilov, "Structure of the thermodynamic Lagrangian density in variational principles of thermodynamics of irreversible processes," VINITI, No. 1066-81.

31. A. I. Gavrilov, I. P. Vyrodov, and E. V. Serdyuk, "Calculation of the critical Rayleigh number in the Benard Problem, based on the generalized variational principle of thermodynamics of irreversible processes," VINITI, No. 1068-81.

32. H. Schlichting, Boundary Layer Theory, McGraw-Hill, New York (1979).