APPLICATION OF THE METHODS OF THERMODYNAMICS OF IRREVERSIBLE PROCESSES TO THE INVESTIGATION OF HEAT AND MASS TRANSFER*

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On the basis of the phenomenological theory—the thermodynamics of irreversible processes—and of the independent results of kinetic and statistical theory, a systematic description is given of transfer phenomena: heat conduction allowing for finite rate of propagation of heat, stress relaxation in viscoelastic media, moisture transfer in capillary-porous media, and turbulent transfer processes. Some solutions are presented for the hyperbolic equation of mass transfer in porous media.

The basic theory. The theory of transfer processes embraces such diverse phenomena as diffusion, heat conduction, thermal diffusion, electrical conduction, absorption of sound waves, etc.

Transfer phenomena occur in systems which, strictly speaking, are not in a state of thermodynamic equilibrium. Two types of transfer processes must be distinguished.

Firstly, there are processes occurring in a system whose initial state is not an equilibrium one; left to itself, the system undergoes transition to this equilibrium state. All relaxation processes are examples of this type.

Secondly, there are processes occurring in a system where external agents (e.g., externally maintained temperature gradients or variable external fields) prevent the establishment of the equilibrium state. In this kind of system, exposed to external influence, there is established, in general, a stationary state which should be distinguished from an equilibrium state.

The study of both types of transfer processes is the task of transfer theory.

The following three basic methods of investigating irreversible transfer processes may be mentioned.

Firstly, there is the kinetic theory, the most direct method of examining irreversible processes. Here some concrete model of the system is assumed initially. The resulting probabilities of the various molecular collisions make it possible to write some kinetic equation, e.g., the Boltzmann equation.

Secondly, the statistical mechanics of irreversible processes offers a very general method. Its objective is the development of a general formalism, similar to the algorithm of the statistical sum in the statistical mechanics of equilibrium states. This formalism must permit the calculation from the ready-made formulas of any macroscopic characteristic of the system in which the irreversible process occurs. Here no special model of the system is assumed beforehand. This approach has fundamental difficulties [1].

Finally, there is the principal method of the present paper. This is to examine transfer processes with the help of the phenomenological theory of the thermodynamics of irreversible processes, a theory which, however, is based on the first two methods.

The thermodynamics of irreversible processes is a powerful phenomenological method of studying heat and mass transfer phenomena. It finds wide application in the investigation of transfer of heat, mass and energy of macroscopic motion. As de Groot [2] has shown, the equations of hydrodynamics of continuous media are obtained directly from the basic equations of thermodynamics of nonequilibrium states. By developing these methods, we can obtain equations for the transfer of energy, heat and mass for various systems, including non-Newtonian liquids and dispersed media, and can also substantiate certain features of turbulent heat and mass transfer theory. This paper will also deal with these questions.

From the thermodynamics of irreversible processes is derived the known formula relating rate of production of entropy d_iS to the fluxes (e.g., heat or diffusion flux, etc.) and to the thermodynamic forces X_i, causing these fluxes (temperature and concentration gradients, etc.):

$$\sigma = \frac{d_iS}{d\tau} = \sum_i J_iX_i \geqslant 0. \tag{1}$$

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In deriving (1), the Gibbs equation

$$TdS = dU + pdV - \sum_i \mu_i dn_i \tag{2}$$

is used. Relations (1) and (2) assume that the entropy of a system not in the equilibrium state is determined by the same independent variables as that of one that is. Postulate (2), which affirms that it is possible to described nonequilibrium states by means of variables defined, strictly speaking, only for equilibrium systems, is not self-evident. However, Prigogine has shown from kinetic theory that it is a very good approximation when the departure from equilibrium is not too great.

For transfer processes, the thermodynamics of irreversible processes, based on (1), is limited to the region of validity of the linear phenomenological laws

$$J_i = \sum_k L_{ik} X_{\bar{k}}, \tag{3}$$

where the phenomenological coefficients L_{ik} are assumed to be constant. This latter fact should be noted particularly, and should be borne in mind when the essentially linear relations (3) nevertheless involve an empirical dependence of the phenomenological coefficients L_{ik} on the variables entering into the definition of the thermodynamic forces. This is, strictly speaking, incorrect within the framework of the thermodynamics of irreversible processes.

Moreover, a reciprocity relation obtains, resulting from microscopic reversibility:

$$L_{ik} = L_{ki}. \tag{4}$$

Conditions (3) and (4) are more rigid than the conditions of applicability of the Gibbs equation. As follows from (1), (3), and (4), it may be asserted that the coefficients are determined by a positive-definite quadratic form of the type $\sum_{ik} L_{ik} X_i X_k \geqslant 0$ for all X_i, specifically for $L_{ii} L_{kk} \geqslant L_{ik}^2$.

In addition, equations (3) must be covariant, i.e., all their terms must have the same tensor dimension.

Usually relations (1)–(4) are applied to a steady transfer process, but they may also be applied, as de Groot has shown, to unsteady phenomena of low intensity.

For intense unsteady transfer processes the phenomenological coefficients entering into (3) cannot be considered constant. The basic requirement of linearity of the phenomenological transfer laws is therefore violated. The linear transfer equations transform in this case to nonlinear equations. The basic relations (1) and (3) then require refinement.

Following Prigogine [3], we shall divide the total change of rate of production of entropy $d\sigma$ in time $d\tau$ into two parts: one part, $d_X\sigma$, is connected with the change of thermodynamic forces, and the other, $d_J\sigma$, with the change of flux:

$$d\sigma = d_X\sigma + d_J\sigma = \sum_i J_i dX_i + \sum_i X_i dJ_i. \tag{5}$$

It has been shown by Prigogine that when the phenomenological coefficients are constant and the reciprocity relation is valid, the portion of the change in rate of entropy increase due to change of thermodynamic forces is equal to the portion due to change of flux l_i.

Consequently,

$$d_X\sigma = d_J\sigma = d\sigma/2, \tag{6}$$

$$\sum_i J_i \frac{dX_i}{d\tau} = \sum_i X_i \frac{dJ_i}{d\tau}. \tag{7}$$

Throughout the region of applicability of the thermodynamics of irreversible processes we have the relation

$$d_X\sigma \leqslant 0. \tag{8}$$

In intense unsteady processes, the fluxes J_i are related with the thermodynamic forces X_k through certain nonlinear equations, whose form, generally speaking, is unknown. However, if the departure from the state of equilibrium is not too great, we may express these nonlinear laws approximately as follows:

$$J_i = L_i^{(r)} \dot{J}_i + \sum_k (L_{ik} X_k + L'_{ik} \dot{X}_k). \tag{9}$$

where $L_i^{(r)}$, L_{ik} and L'_{ik} are constant phenomenological transfer coefficients. In steady transfer phenomena $X_i = J_i \equiv 0$, and then from (9) we obtain the usual linear equation

$$J_i = \sum_k L_{ik} X_k.$$

If the change of thermodynamic forces with time is small, (9) may be written as

$$J_i = L_{ik}^{(r)} \dot{J}_i = \sum_k L_{ik} X_k, \tag{10}$$

where $L_i^{(r)}$ has the dimensions of time and may be called a relaxation coefficient. Such a situation occurs, for example, in heat conduction processes, when the time $L_i^{(r)}$ is comparable with the time taken by the unsteady heat conduction process (see below).

Sometimes we must also take into account terms containing derivatives of the thermodynamic forces with respect to time, for example, in describing the transfer of moisture in capillary-porous substances.

Stress relaxation in viscoelastic media. As a first illustration, and to explain the physical meaning of the additional terms appearing in (10), we shall examine the transfer of momentum of ordered motion in viscoelastic (non-Newtonian) liquids.

A century ago, Maxwell, on the basis of the concept of relaxation, advanced the hypothesis that there is no difference in principle between the mechanical properties of viscous liquids and solid bodies.

Relaxation is the phenomenon of gradual disappearance of elastic stresses under a constant given strain, i.e., the gradual dissipation of elastic energy in the strained body due to its conversion into heat. Relaxation processes are inseparably linked to random thermal motion of the molecules. The shear stresses p_{ik} in a viscoelastic body relax (are dissipated) in a time interval τ_r at some finite rate ω_r.

We shall consider that dissipation of the internal stresses p_{ik} proceeds according to the Maxwell law

$$p_{ik} = p_{ik}(0) \exp(-\tau/\tau_r), \tag{11}$$

where τ_r is the relaxation period, equal to the ratio of viscosity η to shear modulus G ($\tau_r = \eta/G$). Thus, in a viscoelastic body, the shear stresses relax at a rate inversely proportional to viscosity:

$$\dot{p}_{ik} = -p_{ik}/\tau_r = -G p_{ik}/\eta. \tag{12}$$

In an elastic body the shear stresses remain constant $p_{ik} = p_{ik}(0)$), or the period of relaxation $\tau_r \to \infty$. Therefore, if $\tau_r \to \infty$, a liquid behaves like an amorphous solid.

Newtonian liquids may be considered as viscoelastic bodies with relaxation period $\tau_r \to 0$, or with relaxation rate $\omega_r \to \infty$. Consequently, if $\tau_r \to 0$, the substance behaves like an ordinary viscous liquid. For these liquids the friction stress is directly proportional to the viscosity coefficient and to the rate of shear strain ε_{ik} (law of viscous flow). In fact, for plane-parallel flow of an incompressible liquid the friction stress may be written as

$$p_{12} = -\eta \left(\frac{\partial w_1}{\partial x_2} + \frac{\partial w_2}{\partial x_1} \right) \approx -\eta \frac{\partial w_1}{\partial x_2} = \eta \frac{\partial}{\partial \tau} \left(-\frac{\partial l_1}{\partial x_2} \right) = \eta \dot{\varepsilon}_{12}, \tag{13}$$

it being assumed that $\frac{\partial w_1}{\partial x_2} \gg \frac{\partial w_2}{\partial x_1}$.

For intense unsteady flows a viscous liquid behaves like a viscoelastic body. Therefore Newton's law (13) of viscous flow becomes inapplicable. Instead of (13) we must use (10), which, taking the flux to be p_{ik}, $\dot{\varepsilon}_{ik}$ equal to the thermodynamic force, $L_{11} = \eta$ as the viscosity, and $L_1^{(r)} = -\tau_r$ as the relaxation period, may be written as

$$p_{ik} = \eta \dot{\varepsilon}_{ik} - \tau_r \dot{p}_{ik} = \eta \dot{\varepsilon}_{ik} - \eta \dot{p}_{ik}/G. \tag{14}$$

If the relaxation period τ_r is small ($\tau_r = \eta/G \to 0$), we obtain the law of viscous flow from (14), if η is large ($\eta \to \infty$) we obtain from (14) Hooke's law of elasticity

$$\dot{\varepsilon}_{ik} = -\dot{p}_{ik}/G, \tag{15}$$

whence

$$p_{ik} = G\varepsilon_{ik} = \rho w_c^2 \varepsilon_{ik}. \tag{16}$$

Here ω_c is the rate of propagation of shear strain, or the rate of propagation of transverse waves

$$w_c = \sqrt{G/\rho}. \tag{17}$$

For intense unsteady flows the quantity $\tau_r p_{ik}$ is comparable with $\eta\varepsilon_{ik}$, and therefore (14) must be used instead of (13).

For systems of more complex structure the flow law will be given more generally by (9). For example, Oldroyd [4] obtained theoretically the flow equation of a viscoelastic system, consisting of an emulsion and a suspension of one Newtonian liquid in another, in the form

$$p_{ik} = \eta\dot{\varepsilon}_{ik} + \eta'\ddot{\varepsilon}_{ik} - \tau_r \dot{p}_{ik}. \tag{18}$$

The Oldroyd equation is identical with (9) when $L = \eta$, $L' = \eta'$, $L^{(r)} = -\tau_r$. Returning to (10), we note that the additional term $L_i^{(r)}J_i$ describes a finite rate of propagation of the stresses imparted to a body or to a system of bodies.

Heat transfer. Similarly, for intense unsteady transfer processes, instead of the Fourier law of heat conduction

$$J_q = L_{qq}X_q = -\lambda\nabla T \tag{19}$$

we must use relation (10)

$$J_q = L_q^{(r)}\dot{J}_q + L_{qq}X_q, \tag{20}$$

which we shall write in the form

$$\mathbf{q} = -\lambda\frac{\partial T}{\partial \mathbf{n}} - \tau_r\dot{\mathbf{q}}, \tag{21}$$

where λ is the thermal conductivity, and $L_{qq}^{(r)} = -\tau_r$ is the period of relaxation of thermal stress.

Relation (21) was obtained in [7, 8] for the case of heat transfer and diffusion. The rate of propagation of heat is finite:

$$w_q = \sqrt{a/\tau_r} = \sqrt{\lambda/c\rho\tau_r}, \tag{22}$$

where $a = \lambda/c\rho$ is the thermal diffusivity. For nitrogen $\omega_q = 150$ m/sec, and $\tau_r = 10^{-9}$ sec. For metals τ_r is smaller still, for example, $\tau_r = 10^{-11}$ sec for aluminum. Therefore experimental measurement of τ_r is not possible in these cases. However, for gases in conditions of rarefied supersonic flow, the influence of finite rate of progation of heat on heat transfer becomes appreciable.

Equation (21) may be written as

$$\mathbf{q} = -\lambda\frac{\partial T}{\partial \mathbf{n}} - \frac{\lambda}{c\rho w_q^2}\dot{\mathbf{q}}. \tag{23}$$

It is known that the classical theory of heat conduction assumes that the rate of propagation of heat ω_q is infinitely large ($\omega_q \to \infty$). Assuming $\omega_q \to \infty$, we obtain from (23) the Fourier law of heat conduction, which will correspond to the case when the relaxation period of thermal stress is assumed equal to zero ($\tau_r = 0$).

At large rates of change of thermal flux **q**, the second term in (23) becomes comparable with the first and must not be neglected.

If the thermal conductivity is large ($\lambda \to \infty$), or the volume heat capacity is small ($c\rho \to 0$), we obtain from (23)

$$q \sim c\rho w_q^2 T/w_t, \tag{24}$$

where ω_t is the rate of propagation of the isotherm, proportional to the diffusivity. Equation (24) is analogous in form to (16), which describes the state of stress in a body with a very large relaxation period ($\tau_r \to \infty$).

From (23) we can obtain the differential equation of heat transfer. In fact, eliminating the flux q from the heat balance equation for the one-dimensional problem

$$c\rho \frac{\partial T}{\partial \tau} = -\frac{\partial q}{\partial x} \tag{25}$$

and from (23), we obtain

$$\frac{\partial T}{\partial \tau} + \tau_r \frac{\partial^2 T}{\partial \tau^2} = a \frac{\partial^2 T}{\partial x^2}. \tag{26}$$

Equation (25) is of hyperbolic type and takes into account a finite rate of heat propagation.

At low gas pressures, when the volume heat capacity is small ($c\rho \to 0$), heat transfer proceeds by molecular means. In this case the molecular mean free path is determined by the thermal conductivity and the finite rate of heat propagation. Then the first term of (26) may be neglected, and as a result we obtain the heat transfer equation in the form

$$\frac{\partial^2 T}{\partial \tau^2} = w_q^2 \frac{\partial^2 T}{\partial x^2}. \tag{27}$$

This relation will hold for gases in conditions of supersonic flow at low density.

It is shown in Appendix I that the heat transfer equations are hyperbolic if they allow for a finite rate of heat propagation. This result is obtained from the kinetic theory by solving the Boltzmann equation by Grad's method [9].

In conclusion, it is interesting to draw an analogy between published results and a known case of calculation of finite rate of heat propagation – Zel'dovich-Kompaneets temperature waves [10], where the finiteness of the rate of heat propagation appears because of the dependence (stepwise) of the thermophysical properties of the medium on temperature.

Mass transfer in colloidal capillary-porous bodies. Moist materials are hydrophilic capillary-porous substances. In these substances osmotically-bound moisture and absorption-bound moisture are transferred by molecular means in conformity with Fick's law of diffusion. As in the case of molecular heat transfer, it is assumed that the rate of motion of mass is infinitely great. In analytical diffusion theory this assumption does not affect the final results, since the relaxation period in molecular mass transfer is approximately of the same order as the relaxation period for heat transfer.

However, in addition to the diffusion of moisture, in colloidal capillary-porous substances there is a rather slow movement of moisture under the influence of capillary forces. Usually capillary motion of moisture in polycapillary-porous substances is described formally by a moisture transfer law analogous to that for diffusion (capillary diffusion). It is assumed that the capillary potential is a continuous function of the moisture content of the substance, and then the gradient of capillary potential will be proportional to the moisture content gradient. Therefore, the flux of capillary moisture j_{cap} will be

$$j_{\text{cap}} = k \nabla \psi, \tag{28}$$

where

$$k = \frac{\rho^2}{8\eta} \int_{r_0}^{r} r^2 f(r)\, dr, \tag{29}$$

and $f(r)$ is the differential curve of pore distribution along the radius r, which varies in the body from some minimum capillary radius r_0 to a maximum r for given moisture content u (maximum radius of capillaries filled with liquid).

Under isothermal conditions the gradient of capillary potential $\nabla\psi$ is directly proportional to the gradient ∇u, of moisture content, and then we may write

$$j_{\text{cap}} = -D_{\text{cap}} \rho_0 \nabla u, \tag{30}$$

where

$$D_{\text{cap}} = \frac{\sigma \cos \vartheta}{4\eta r^2 f(r)} \int_{r_0}^{r} r^2 f(r)\, dr, \tag{31}$$

σ being the surface tension and ϑ the contact angle of the liquid on the capillary walls.

Equation (30) is valid for a porous body of polycapillary structure. For a monocapillary body $f(r) \to \infty$, hence $k \to \infty$, and $\nabla\psi \to \infty$. In this case the capillary moisture flux will be

$$\mathbf{j}_{\mathrm{cap}} = \Pi \rho b \mathbf{w}_{\mathrm{cap}}, \tag{32}$$

where W_{cap} is the average velocity of the liquid in a body with monocapillary structure.

Equation (30) is analogous to the Fick formula for diffusion of osmotic moisture, where it is assumed that the rate of propagation of moisture, like the propagation of heat, is infinitely great. In fact, in colloidal capillary-porous bodies the velocity of the moisture (liquid) is of the order $2 \cdot 10^{-2}$ to $5 \cdot 10^{-2}$ m/sec, and the moisture diffusion coefficient D_m for different substances varies from $1.4 \cdot 10^{-8}$ to $30 \cdot 10^{-8}$ m^2/sec [11]. Therefore, the relaxation period τ_{rm} will be of the order $(0.4\text{–}1.2) \cdot 10^{-4}$ sec, i.e., approximately 10^5 to 10^7 times greater than τ_r for heat transfer in gases and metals.

Thus, to describe moisture transfer in colloidal capillary-porous bodies of polycapillary structure, the general moisture transfer law (10) must be used, i.e.,

$$\mathbf{j} = -D_m \rho_0 \nabla u - \tau_{rm} \partial \mathbf{j}/\partial\tau, \tag{33}$$

where

$$\tau_{rm} = D_m/w_{rm}^2.$$

If the capillary walls are slightly hydrophilic, the capillary moisture diffusion coefficient may be considered to be very large. Then we obtain from (33)

$$-\rho_0 \frac{\partial u}{\partial n} - \frac{1}{w_{rm}^2} \frac{\partial j}{\partial \tau} = \frac{j}{D_m} \to 0. \tag{34}$$

We shall designate the linear rate of displacement of the iso-concentration surface (surface inside the body with the same relative concentration u) by $\omega_u = dn/d\tau$. From (34) we obtain

$$j = \rho_0 w_{rm}^2 \Delta u / w_u, \tag{35}$$

where Δu is some given moisture content difference.

For a porous substance of monocapillary structure we may approximately take $\omega_{rm} = \omega_u$, and Δu will be equal to the maximum moisture content $u_\infty (\Delta u = u_\infty)$; then from (35) we obtain

$$j = \rho_0 w_{rm} u_\infty, \tag{36}$$

i.e., relation (32), since in this case $\rho_0 u_\infty = \Pi \rho b$.

Consequently, for a monocapillary-porous substance, the transfer velocity ω_{rm} is approximately equal to the rate of capillary motion ($\omega_{rm} = \omega_{\mathrm{cap}}$).

In addition, it follows from the above analysis that (33) describes moisture diffusion at a finite rate of moisture propagation conditioned by capillary absorption.

From the law of conservation of mass of moisture for the one-dimensional problem we have

$$\rho_0 \frac{\partial u}{\partial \tau} = -\frac{\partial j}{\partial x}. \tag{37}$$

If we replace j by (33) and assume $\tau_{rm} = D_m/\omega_{rm}^2$ to be constant, we obtain the differential equation of mass transfer in colloidal capillary-porous bodies*:

$$\frac{\partial u}{\partial \tau} + \tau_{rm} \frac{\partial^2 u}{\partial \tau^2} = D_m \frac{\partial^2 u}{\partial x^2}. \tag{38}$$

This equation differs from the usual moisture conduction equation in having the additional term $\tau_{rm}\, \partial^2 u/\partial\tau^2$, which describes the capillary motion of moisture.

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*The case when the rate of capillary motion ω_{rm} depends on the coordinates is examined in Appendix II.

In the case of nonisothermal conditions, the differential equation of moisture transfer in colloidal capillary-porous bodies takes the form

$$\frac{\partial u}{\partial \tau} + \tau_{rm} \frac{\partial^2 u}{\partial \tau^2} = D_m \left(\frac{\partial^2 u}{\partial x^2} + \delta \frac{\partial^2 t}{\partial x^2} \right), \tag{39}$$

where δ is the thermal gradient coefficient, namely, the ratio of the moisture thermal diffusion coefficient to the moisture diffusion coefficient.

This equation must be solved together with the heat conduction equation for a moist body

$$\frac{\partial T}{\partial \tau} = a \frac{\partial^2 T}{\partial x^2} + \epsilon \frac{L}{c} \frac{\partial u}{\partial \tau}, \tag{40}$$

where L is the specific heat of phase transition, and ϵ is the phase transition parameter.

The set of differential equations (39)–(40) has been solved by A. V. Luikov and T. L. Perel'man for the boundary conditions

$$T(x, 0) = T_0, \quad T(0, \tau) = T_a, \tag{41}$$

$$\frac{\partial T(\tau, \infty)}{\partial x} = 0, \quad u(x, 0) = u_0, \tag{42}$$

$$\frac{\partial u(0, \tau)}{\partial \tau} = 0, \quad u(0, \tau) = u_a, \tag{43}$$

$$\frac{\partial u(\tau, \infty)}{\partial x} = 0. \tag{44}$$

Analysis of the solution obtained indicates that thermal diffusion of moisture proves to have an appreciable influence on capillary moisture transfer at finite rate ω_{rm}. To illustrate this, we present the solution of the above problem (39)–(44) for the particular case of isothermal conditions of moisture transfer $\delta = 0$ with no phase transitions $\epsilon = 0$. In this case the solution may be written as

$$u^* = \frac{u - u_0}{u_a - u_0} =$$

$$= E(\tau^* - \xi) \left[1 - \frac{1}{\pi} \int_0^1 \exp(-\tau^* z) \sin\left(\sqrt{z(1-z)}\,\xi\right) \frac{dz}{z} \right], \tag{45}$$

where $\tau^* = \tau/\tau_{rm}$ is dimensionless time,

$$\xi = x/\sqrt{D_m \tau_{rm}}, \tag{46}$$

and

$$E(\tau^*) = \begin{cases} 0 \text{ when } \tau^* < 0 \\ 1 \text{ when } \tau^* > 0. \end{cases} \tag{47}$$

Equation (45) describes moisture transfer with finite velocity (when $\tau^* > \xi$). The moisture reaches point x no earlier than time $\tau \geqslant \sqrt{\tau_{rm}/D_m}\, x$, when there is still no moisture $[E(\tau^* - \xi) = 0]$ at points more remote from the surface. The solution of this problem with infinite moisture transfer rate ($\tau_{rm} = 0$), is known to have the form

$$u^* = \operatorname{erfc}(x/2\sqrt{D_m \tau}). \tag{48}$$

This solution (48) differs from (45); they coincide only when $\tau \to \infty$. From (45) as $\tau^* \to \infty$ we obtain

$$u^* = 1 - \frac{\eta}{\sqrt{\pi \tau^*}} + \ldots = 1 - \frac{x}{\sqrt{\pi D_m \tau}} + \ldots, \tag{49}$$

which is identical to (38) when $\tau \to \infty$.

Thus, the general relations of thermodynamics of irreversible unsteady transfer processes may be used to describe diffusion-capillary moisture transfer in moist materials.

In concluding this section, we note that estimates indicate that in a number of cases of moisture transfer in complex and intertwined systems of capillaries, such as exist in a capillary-porous body, we must also take account of terms containing derivatives of the thermodynamic forces with respect to time (9).

Turbulent heat and mass transfer processes. Transfer process of various types (heat, momentum, and mass) play a major role in turbulent flow. Following the general viewpoint adopted in the present paper, we give below a very brief resume, because of insufficient space, of the results obtained from the theory of transfer processes in turbulent media, allowing for finite velocity of propagation of the respective quantities. New results from the description of turbulent transfer processes will be published separately.

A distinctive feature of transfer processes in turbulent flow is the range of scales of motion of the turbulent medium, responsible for mixing. The nature of turbulent transfer is determined by the distribution of energy between turbulent motions of different scale. The largest scale of motion, to which almost all the flow energy contributes, is called the scale of turbulence l. Values of the velocity of a liquid at points whose distances apart do not exceed l, prove to be statistically interrelated. Therefore, particles of liquid or of additive whose distance apart does not exceed l, will not move independently. This upsets the analogy between turbulent and molecular transfer.

However, as a rule, the dimensions of the regions in which the transfer processes occur are appreciably greater than the scale of turbulence. In such cases it is justifiable to describe turbulent transfer by analogy with molecular transfer, taking into account certain peculiarities, on which we dwell below.

We shall thus examine how far to stretch the analogy between molecular transfer and transfer processes under conditions of small-scale turbulence [12].

Random molecular motion may be described by a mean molecular velocity v_m and a mean molecular free path l_m. The diffusion coefficient (or, in the case of heat transfer, the thermal conductivity) is defined in terms of these quantities as

$$D_m \sim v_m l_m, \tag{50}$$

using the concept of a constant of proportionality between the flow of matter (heat) and concentration (temperature) of its gradient.

Similarly, random turbulent motion may be described by a mean value v of the turbulent velocity fluctuations (fluctuations of the intensity of turbulence and of the scale of turbulence l of the type introduced in the Prandtl "mixing length"). We can determine the coefficient of turbulent diffusion

$$D_T \sim vl, \tag{51}$$

which is the coefficient of proportionality between the mean turbulent flux of the quantity being transferred and its average concentration gradient

$$J = -D_T \rho \nabla \bar{c}, \tag{52}$$

where

$$J = \overline{\rho c' v'} \tag{53}$$

(the primes indicate deviation from mean values).

If a diffusion law expressed by (30) is assumed, then, using the continuity equation for the quantity being transferred, we obtain a diffusion equation in the usual form (parabolic). There is, however, a vast difference in the scales of motion between molecular and turbulent processes. For example, for molecular diffusion

$$v_m \sim 10^4 \text{ cm/sec} \quad l_m \sim 10^{-5},$$
$$D_m \sim 10^{-1} \text{ cm}^2/\text{sec} \quad \tau_m \sim 10^{-9} \text{ sec}.$$

For turbulent motion, acceptable values of turbulent fluctuations are ~10% of the mean velocity and lie in the ranges

$$v \sim 1-10^2 \text{ cm/sec} \quad l \sim 1-10^3 \text{ cm}.$$

Hence

$$D_T \sim 1-10^5 \text{ cm}^2/\text{sec},$$
$$\tau_r \sim 10^{-3}-10^3 \text{ sec}.$$

From the estimates given, it follows, firstly, that in the majority of problems of turbulent transfer molecular processes may be neglected $D_T \gg D_M$.

Secondly, it appears that there is an even greater qualitative difference in the description of turbulent transfer processes, since, because of the vast difference in scales and velocities of motion, the parabolic equations commonly used to describe molecular transfer processes, and introduced under the assumption that the velocity of the molecules is infinite, become unsuitable. The applicability of the parabolic transfer equations is the more restricted, the less the effective velocities of the diffusing substance (heat).

Thus, the parabolic equation of turbulent diffusion, which indicates that any disturbance is instantaneously apparent, if only to a minute extent, at an arbitrarily great distance from its source, should be replaced by a hyperbolic transfer equation.

Again using the relations of thermodynamics of irreversible processes between fluxes and thermodynamic forces, as modified earlier for unsteady processes, we have, for the case of isotropic turbulence,

$$\tau_r \frac{\partial^2 C}{\partial \tau^2} + \frac{\partial C}{\partial \tau} = D_T \frac{\partial^2 C}{\partial y^2}. \tag{54}$$

If D_T is variable, the term on the right has the form $\frac{\partial}{\partial y}\left(D_T \frac{\partial C}{\partial y}\right)$.

Equation (54) was introduced by Goldstein [13] (see also [14]) through an examination of a known random-walk problem. The same generalization has been proposed for non-isotropic turbulence.

In the random-walk problem Markovian stochastic processes of various orders may be examined.

The usual diffusion equation can easily be derived from the assumption that the diffusing particles move randomly, i.e., their coordinates vary with time according to the law of a Markovian stochastic process of the first order. Then the diffusion equation is the Kolmogorov equation for this stochastic process.

This scheme proves to be inadequate and too simple to be applied to turbulent transfer processes. The probability of locating a particle of the substance being transferred under turbulent transfer conditions depends at any moment of time τ not only on its position at the immediately previous moment of time, but also on some part of the previous trajectory of the particle. If we restrict attention to a Markov process of second order, we obtain a transfer equation of hyperbolic type.

There also exists another, simpler derivation of the hyperbolic transfer equation from the generalized Fokker-Planck equation in phase space [15].

In conclusion, we stress the following: equation (54) is hyperbolic; this shows that the term $\tau_r \frac{\partial^2 C}{\partial \tau^2}$ is important, independently of its order, since it contains the higher derivative, and therefore determines the type of the equation and changes the qualitative nature of the solution. Let us compare the behavior of solutions of parabolic and hyperbolic transfer equations when, for example, at time zero in an infinite space there is a source of the type

$$C(0, y) = C_0 \delta(y). \tag{55}$$

We have

$$C_p(y, \tau) = \frac{C_0}{\sqrt{4\pi D_T \tau}} \exp\left(-\frac{y^2}{2D_T \tau}\right), \tag{56}$$

and from (54) it follows, correspondingly, that

$$C_h(y, \tau) = C_0 \begin{cases} A \text{ when } y < \left(\frac{\mathrm{Pr}}{\tau_r}\right)^{1/2} \tau \\ 0 \text{ when } y > \left(\frac{D_T}{\tau_r}\right)^{1/2} \tau, \end{cases} \tag{57}$$

where

$$A = \frac{1}{4\tau_0} \exp\left(-\frac{\tau}{2\tau_0}\right)\left[I_0(Y) + \frac{\tau}{2\tau_r}\,\frac{I_1(Y)}{Y}\right],$$
$$Y = \frac{1}{2\sqrt{\tau_0}}\sqrt{\frac{\tau^2}{\tau_r} - \frac{y^2}{D_T}},$$

and $I_0(Y)$ and $I_1(Y)$ are modified Bessel functions of order 0 and 1. At small times the behavior of solutions (56) and (57) are appreciably different. We note, for example, the basic fact, which may be seen from (56), that diffusion takes place according to the law $\sqrt{\overline{y^2}} \sim \sqrt{\tau}$, while from (57) $\sqrt{\overline{y^2}} \sim \tau$ is obtained. When $\tau \to \infty$, (56) approaches (57) asymptotically.

We make several comments on the possibility of generalizing hyperbolic transfer equations in the case of more than one (space) measurement.

To derive the transfer equations with allowance for finite velocity of propagation of the transferred substance in the three-dimensional case, we must examine the appreciably more complex three-dimensional (or two-dimensional) Markov process. It can be shown that the transfer equation will then be not a differential, but an integro-differential one. The integral operator in this equation cannot always be represented in the form of derivatives with respect to time of various orders. It may be shown (we omit this owing to insufficient space) that, for example, in the simplest case of two-dimensional diffusion, the turbulent transfer equation may be put in the form of a differential equation of type (54) only if $\tau_r(x) = \tau_r(y)$, which will hold, for example, in isotropic turbulence.

In concluding, we note that methods of thermodynamics of irreversible processes are valuable for investigation of interrelated heat and mass transfer processes. Further development of these methods applicable to intense unsteady transfer processes is an urgent and important task in the over-all problem of heat and mass transfer.

Appendix I

It is known that the Boltzmann equation is valid for a rarefied gas in which only two-body collisions between molecules are possible. In the absence of external forces it takes the form

$$\frac{\partial f}{\partial \tau} + \vec{\xi}\,\frac{\partial f}{\partial \mathbf{x}} = \frac{1}{m}\,J_c. \tag{1}$$

Here $f(\mathbf{x}, \vec{\xi}, \tau)$ is the mass density distribution function, and J_c is the collision integral which depends on the law of molecular interaction.

Grad has proposed the use of an expansion of the distribution function f in Hermite polynomials, taking as weighting function the equilibrium Maxwell function $f^{(0)}$:

$$f = f^{(0)} \sum_{n=0}^{\infty} \frac{1}{n!}\, a_i^{(n)} H_i^{(n)}. \tag{2}$$

Substitution of this expansion in the Boltzmann equation leads to an infinite system of differential equations. The required degree of approximation to the complete solution of the Boltzmann equation is determined by the number of terms taken in the expansion. In order to obtain a finite system of differential equations in closed form, all the Hermite coefficients of higher order are assumed to be zero.

Most attention has been given to the third approximation, when the first three terms in the expansion of the distribution function are examined:

$$f = f^{(0)} \sum_{i,j,k}\left(1 + \frac{1}{2}\, a_{ij}^{(2)} H_{ij}^{(2)} + \frac{1}{6}\, a_{igk}^{(3)} H_{ijk}^{(3)}\right). \tag{3}$$

The Hermite coefficients $a_{ij}^{(2)}$ and $a_{ijk}^{(3)}$ are related to the moments of the distribution function of second and third order

$$a_{ij}^{(2)} = \frac{p_{ij}}{p}, \quad a_{ijk}^{(3)} = \frac{S_{ijk}}{\rho\sqrt{RT}},$$

where p_{ij} is the stress tensor. The convolute third moment $S_i = \sum_j S_{ijj}$, which is equal to twice the heat flux q_i, has an important physical meaning.

Therefore, instead of approximation (3) we use the incomplete third approximation

$$f = f^{(0)} \sum_{i,j} \left(1 + \frac{1}{2}\, a_{ij}^{(2)} H_{ij}^{(2)} + \frac{1}{10}\, a_i^{(3)} H_i^{(3)}\right), \quad a_i = \sum_{j,k} a_{ijk}, \tag{4}$$

which may be written in the form

$$f = f^{(0)} \sum_{i,j} \left\{1 + \frac{p_{ij}}{2pRT}\, c_i c_j - \frac{q_i}{RT}\, c_i \left(1 - \frac{c^2}{5RT}\right)\right\}, \tag{5}$$

$$c_i = \xi_i - w_i.$$

Thus, the components of moments ρ, T, ω_i, p_{ij}, q_l — the total number is 13 — are taken as parameters of state of the system. The stresses and the heat flux are examined along with the variables ρ, T, ω_i.

In the system of equations of the 13 moments there appear the equations of conservation of mass, momentum and energy, as well as the equations for the stresses and the heat flux:

$$\frac{\partial \rho}{\partial \tau} + \sum_r \frac{\partial}{\partial x_r}\, (\rho w_r) = 0, \tag{6}$$

$$\frac{\partial w_i}{\partial \tau} + \sum_r \left(w_r \frac{\partial w_i}{\partial x_r} + \frac{1}{\rho}\, \frac{\partial P_{ir}}{\partial x_r}\right) = 0, \tag{7}$$

$$\frac{\partial p}{\partial \tau} + \sum_{i,r} \left\{\frac{\partial}{\partial x_r}\, (w_r p) + \frac{2}{3}\, p_{ir}\, \frac{w_i}{\partial x_r} + \frac{2}{3}\, \frac{\partial q_r}{\partial x_r}\right\} = 0, \tag{8}$$

$$\begin{aligned} \frac{\partial p_{ij}}{\partial \tau} + \sum_{r,s} \Bigg\{ & \frac{\partial}{\partial x_r}\, (w_r p_{ij}) + \frac{2}{5} \left(\frac{\partial q_i}{\partial x_j} + \frac{\partial q_j}{\partial x_i} - \frac{2}{3}\, \delta_{ij} \frac{\partial q_r}{\partial x_r}\right) + \\ & + p_{ir}\, \frac{\partial w_j}{\partial x_r} + p_{jr}\, \frac{\partial w_i}{\partial x_r} - \frac{2}{3}\, \delta_{ij}\, p_{rs}\, \frac{\partial w_r}{\partial x_s} + p \left(\frac{\partial w_i}{\partial x_j} + \frac{\partial w_j}{\partial x_i} - \right. \\ & \left. - \frac{2}{3}\, \delta_{ij} \frac{\partial w_r}{\partial x_r}\right)\Bigg\} + \beta\rho\, p_{ij} = 0, \end{aligned} \tag{9}$$

$$\begin{aligned} \frac{\partial q_i}{\partial \tau} + \sum_r \Bigg\{ & \frac{\partial}{\partial x_r}\, (w_r q_i) + \frac{7}{5}\, q_r\, \frac{\partial w_i}{\partial x_r} + \frac{2}{5}\, q_r\, \frac{\partial w_r}{\partial x_i} + \frac{2}{5}\, q_i\, \frac{\partial w_r}{\partial x_r} + \\ & + RT\, \frac{\partial \rho_{ir}}{\partial x_r} + \frac{7}{2}\, p_{ir}\, \frac{\partial RT}{\partial x_r} - \frac{p_{ir}}{\rho}\, \frac{\partial P_{rs}}{\partial x_r}\Bigg\} + \\ & + \frac{5}{2}\, p\, \frac{\partial RT}{\partial x_i} + \frac{2}{3}\, \beta\rho\, q_i = 0, \end{aligned} \tag{10}$$

where

$$p_{ij} = P_{ij} - p\delta_{ij}.$$

Here β is the collision parameter. The equations of the 13 moments are hyperbolic. The derivatives with respect to time appearing in them require the assignment of definite initial conditions.

In the case of slowly varying flows the dependence on the initial values may be neglected. The time to establish steady (quasi-equilibrium) flow is much less than the time for the system to reach the equilibrium state. In cases when these two time scales are comparable, the flow must not be considered steady; here the derivative with respect to time must play an important role.

We shall examine, as an example, the unsteady heat flux in a stationary gas ($w = 0$), when p_{ij} and q_i depend only on time. We arrive at the following system of equations

$$\partial \rho / \partial \tau = 0, \tag{11}$$

$$\sum_r \partial P_{ir} / \partial x_r = 0, \tag{12}$$

$$\partial p / \partial \tau = 0, \tag{13}$$

$$\partial p_{ij} / \partial \tau + \beta \rho \, p_{ij} = 0, \tag{14}$$

$$\frac{\partial q_i}{\partial \tau} + \sum_r \left\{ \frac{7}{2} \, p_{ir} \, \frac{\partial RT}{\partial x_r} \right\} + \frac{5}{2} \, p \, \frac{\partial RT}{\partial x_i} + \frac{2}{3} \, \beta \rho \, q_i = 0. \tag{15}$$

It follows that the pressure p is constant; the stresses p_{ij} are damped exponentially

$$p_{ij}(\tau) = p_{ij}(0) \exp(-\beta \rho \tau). \tag{16}$$

From the latter equation we obtain for the heat flux

$$\frac{\partial q_i}{\partial \tau} + \sum_r \left\{ \frac{7}{2} p_{ir} + \frac{5}{2} \, p \delta_{ir} \right\} \frac{\partial RT}{\partial x_r} + \frac{2}{3} \, \beta \rho \, q_i = 0. \tag{17}$$

This may also be written in the form

$$q_i + \frac{1}{(2/3)\beta \rho} \, \frac{\partial q_i}{\partial \tau} = \\ = - \sum_r \left\{ \left(\frac{15}{4} \, \frac{pR}{\beta \rho} \delta_{ir} + \frac{21}{4} \, \frac{R}{\beta \rho} \, p_{ir} \right) \frac{\partial T}{\partial x_r} \right\}, \tag{18}$$

which coincides with (21). The quantity $\lambda = \frac{15}{4} \frac{pR}{\beta\rho}$ is the thermal conductivity, which customarily appears in the system of equations for a continuous medium. The value $\frac{1}{(2/3)\,\beta\rho}$ has the significance of a relaxation time.

Appendix II

For a number of capillary-porous bodies the rate of capillary motion of moisture ω_{cap}, as the work of S. Taneeva has shown, is inversely proportional to the path x, $\omega_{\text{cap}} = a_0/x$, where a_0 is some constant value depending on the porosity of the body, its capillary properties, and the viscosity of the liquid. Assuming in the first approximation that $\omega_{\text{cap}} = \omega_{\text{rm}}$, we obtain for the moisture flux the following relation

$$j = -D_m \rho_0 \frac{\partial u}{\partial x} - \frac{D_m x^2}{a_0^2} \, \frac{\partial j}{\partial \tau}. \tag{19}$$

Using the moisture balance equation

$$\rho_0 \, \frac{\partial u}{\partial \tau} = - \frac{\partial j}{\partial x}, \tag{20}$$

we obtain the differential equation of moisture transfer under isothermal conditions for a flux density of the following form

$$\frac{\partial j}{\partial \tau} + \frac{D_m}{a_0^2} \, x^2 \, \frac{\partial^2 j}{\partial \tau^2} = D_m \, \frac{\partial^2 j}{\partial x^2}. \tag{21}$$

We shall examine the boundary problem for a semi-infinite body, when a constant moisture flux j_0 crosses the exposed surface:

$$j(0, \tau) = j_0, \quad j(\infty, \tau) = 0; \tag{22}$$

$$j(x, 0) = 0, \quad \frac{\partial j(0, x)}{\partial \tau} = 0. \tag{23}$$

We shall seek a solution in the form

$$j(x, \tau) = j_0 f(\xi), \tag{24}$$

where

$$\xi = 2a_0 \tau / x^2. \tag{25}$$

In this case we obtain the differential equation

$$(\xi^2 - 1) f''(\xi) + \left(\frac{3}{2}\xi - \frac{a_0}{2D_m}\right) f'(\xi) = 0 \tag{26}$$

with the conditions

$$f(\infty) = 1, \quad f(0) = 0, \quad f'(0) = 0. \tag{27}$$

The solution of (26) with initial conditions (27) may be written as

$$f(\xi) = 0 \text{ when } 0 \leqslant \xi < 1,$$

$$f(\xi) = \sqrt{\frac{2}{\pi}} \frac{\Gamma(\alpha + 3/4)}{\Gamma(\alpha + 1/4)} \int_1^{\xi} \frac{(\eta - 1)^{\alpha - 3/4}}{(\eta + 1)^{\alpha + 3/4}} \, d\eta,$$

where $\alpha = a_0/4D_m$ – the integral appearing in (28) – may be expressed in terms of hypergeometric functions. The cases $\alpha \gg 3/4$ and $\alpha \ll 3/4$ may easily be investigated, and, for example, in the particular case $\alpha = 3/4$ we obtain

$$j(x, \tau) = j_0 \begin{cases} 0 & \text{when } x^2 > 2a_0\tau \\ 1 - x\sqrt{2/(x^2 + 2a_0\tau)} & \text{when } x^2 < 2a_0\tau. \end{cases} \tag{29}$$

Appendix III

The solution of the system of differential equations (39)-(40) with boundary conditions (41)-(44) in the absence of phase transitions ($\varepsilon = 0$) has the form

$$u^* = \frac{u - u_0}{u_a - u_0} = E(\tau^* - \xi)\left\{\left[1 - \frac{\mathrm{Lu\,Pn}}{1 - \mathrm{Lu}}(1 - \exp[-(1 - \mathrm{Lu}) \times \right.\right.$$

$$\left. \times (\tau^* - \xi)])\right] \exp\left(-\frac{1}{2}\xi\right) + \frac{1}{2}\xi \int_{\xi}^{\tau^*} \left[1 - \frac{\mathrm{Lu\,Pn}}{1 - \mathrm{Lu}}(1 - \exp[- \right.$$

$$\left.\left. - (1 - \mathrm{Lu})(\tau^* - v)])\right] \exp\left(-\frac{1}{2}v\right) \frac{I_1\left[(1/2)\sqrt{v^2 - \xi^2}\right]}{\sqrt{v^2 - \xi^2}} \, dv \right\} +$$

$$+ \mathrm{Lu\,Pn} \int_0^{\tau^*} \exp[-(1 - \mathrm{Lu})(\tau^* - v)] \operatorname{erfc}(1/2\sqrt{v}) \, dv, \tag{30}$$

where

$$E(\tau^*) = \begin{cases} 0 \text{ when } \tau^* < 0 \\ 1 \text{ when } \tau^* > 0, \end{cases}$$

$$\xi = x / \sqrt{D_m \tau_{rm}},$$

and $I_1(v)$ is a modified Bessel function of first order. The last term of (30) differs from zero when $\tau^* > 0$ and describes the thermal diffusion transfer of moisture. If moisture transfer occurs at constant temperature, the Pn number is zero (Pn = 0). Then from the solution of (30) we obtain

$$u^* = E(\tau^* - \xi)\left[\exp\left(-\frac{1}{2}\xi\right) + \frac{1}{2}\xi \int_{\xi}^{\tau^*} \exp\left(-\frac{1}{2}v\right) \frac{I_1\left[(1/2)\sqrt{v^2 - \xi^2}\right]}{\sqrt{v^2 - \xi^2}} \, dv\right]. \tag{31}$$

This solution (31) may be written in another form

$$u^{*} E(\tau^{*} - \xi) \left\{1 - \frac{1}{\pi} \int_{0}^{1} \exp(-\tau^{*} z) \sin\left(\sqrt{z(1-z)}\,\xi\right) \frac{dz}{z}\right\}, \tag{32}$$

which was given above (see Eq. (45)).

Notation

a – thermal diffusivity ($a = \lambda / c\rho$); b – capillary fill factor; c – specific heat; C – concentration; D_{cap} – capillary diffusion coefficient; D_m – moisture diffusion coefficient or mass diffusion coefficient in a moving mixture of gases; D_T – coefficient of turbulent diffusion; ϵ – phase transition parameter; G – shear modulus; I – specific heat and mass flux; k – coefficient of capillary conduction; n – direction of normal to isothermal surface; n_i – concentration of i-th component in the mixture; p – pressure or friction stress; $p = dp/d\tau$ – rate of change of friction stress with time; q – specific heat flux; $q = dp/d\tau$ – rate of change of specific heat flux with time; L – specific heat of phase transition; S – entropy; T – temperature; v_m – velocity of molecules; u – internal energy or relative moisture concentration in the porous body (moisture content); ω – velocity of liquid (gas), or rate of propagation of stress, heat and mass; X_l – thermodynamic motive forces; ε – shear strain; $\varepsilon = d\varepsilon/d\tau$ – shear strain rate; η – viscosity; ϑ – contact angle; λ – thermal conductivity; μ_i – chemical potential of i-th component of mixture; Π – porosity; ρ – density; ρ_0 – density of absolutely dry substance; σ – entropy increase or surface tension; τ_{rm} – period of propagation of moisture in capillary-porous system; ψ – capillary potential; Lu – inertia number of moisture content field relative to temperature field in a porous body ($Lu = D_m/a = D_m\, c\rho_0/\lambda$); Pn – Posnov number ($Pn = \delta(u_a - u_0)/(T_a - T_0)$). Subscripts: q – thermal state; c – elastic state; m – characteristic of mass or molecular characteristics; r – relaxation characteristics; T – turbulent properties; t – isothermal state.

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