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THE THERMODYNAMIC ANALYSIS OF MASS-TRANSFER MOTIVE FORCES IN THE COURSE OF CRYSTALLIZATION FROM SOLUTIONS

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On the basis of taking the volume, mass, momentum, and energy of the surface phase into account, the structure of the motive forces of mass transfer to the phase interface (and from it into the carrier phase) in crystallization and solution is established. The correctness of the relations obtained is verified in two systems.

1. Structure of Dissipative Function of a Multiphase Medium in Which Crystallization Occurs

In accordance with the concepts outlined in [1], a multiphase medium is considered, where the first (carrier) medium is a solution, the  $r$ -th is crystals, of dimensions in the range  $(r - dr, r + dr)$ , and the surface phase is a  $\sigma$  phase (the  $\sigma$  phase is of volume  $V_\sigma$ , density  $\rho_\sigma^0$ , and temperature  $T_\sigma$ ). In the steady case, the intensity of mass transfer from the carrier phase into the  $\sigma$  phase and from the  $\sigma$  phase into the  $r$ -th phase is the same. In the most general case, however, the fluxes through the surface phase may be unequal; in other words

$$\rho_2^0 f \lambda dr \neq J_{1\sigma} f dr, \quad \rho_2^0 f \xi dr \neq J_{\sigma 1} f dr.$$

Let  $\eta = \lambda - \xi$ ,  $J = J_{1\sigma} - J_{\sigma 1}$ . By means of a discussion analogous to that outlined in [1], the following equations are obtained in differential form: mass conservation of the carrier phase

$$\frac{\partial \rho_1}{\partial t} + \text{div}(\rho_1 \mathbf{v}_1) = - \int_0^R J f dr, \tag{1}$$

mass conservation of the component in the carrier phase (in the interests of simplicity of exposition, it is assumed that only one component takes part in the phase transition)

$$\rho_1 \frac{d_1 c_{k1}}{dt} = (c_{k1} - 1) \int_0^R J f dr, \tag{2}$$

the balance of number of particles

$$\frac{\partial f}{\partial t} + \text{div}(f \mathbf{v}_2) + \frac{\partial f \eta}{\partial r} = 0, \tag{3}$$

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mass conservation of the  $\sigma$  phase

$$\frac{D_2 \rho_\sigma^0 V_\sigma}{Dt} = J - \rho_2^0 \eta, \quad (4)$$

mass conservation of the component in the  $\sigma$  phase

$$\rho_\sigma^0 V_\sigma \frac{D_2 c_{k\sigma}}{Dt} = (1 - c_{k\sigma}) (J - \rho_2^0 \eta), \quad (5)$$

motion of the carrier phase

$$\rho_1 \frac{d_1 \mathbf{v}_1}{dt} = -\alpha_1 \nabla P - \int_0^R (\rho_2^0 r + \rho_\sigma^0 V_\sigma) f \mathbf{f}_{12} dr - \int_0^R J f (\mathbf{v}_2 - \mathbf{v}_1) dr + \rho_1 \mathbf{F}_1, \quad (6)$$

motion of the  $r$ -th phase

$$(\rho_2^0 r + \rho_\sigma^0 V_\sigma) f \frac{D_2 \mathbf{v}_2}{Dt} = (r + V_\sigma) f \nabla P + (\rho_2^0 r + \rho_\sigma^0 V_\sigma) f \mathbf{f}_{12} + (\rho_2^0 r + \rho_\sigma^0 V_\sigma) f \mathbf{F}_2 \quad (7)$$

(the velocity of motion of the  $\sigma$  phase consisting of particles of dimension  $r$  is assumed to be the same as the velocity of motion of the particles themselves), energy of the carrier phase

$$\rho_1 \frac{d_1 u_1}{dt} = \frac{\alpha_1 P}{\rho_1^0} \frac{d \rho_1^0}{dt} + \int_0^R (\rho_2^0 r + \rho_\sigma^0 V_\sigma) \mathbf{f}_{12} (\mathbf{v}_1 - \mathbf{v}_2) dr - \int_0^R J f \frac{(\mathbf{v}_2 - \mathbf{v}_1)^2}{2} dr - \nabla q_1 - \int_0^R q_{1\sigma} dr + \rho_1 Q_1, \quad (8)$$

energy of the  $r$ -th phase

$$\rho_2^0 r f \frac{D_2 u_2}{Dt} = f \frac{rP}{\rho_2^0} \frac{D_2 \rho_2^0}{Dt} - q_{2\sigma} + \rho_2^0 Q_2 f r, \quad (9)$$

energy of the  $\sigma$  phase

$$\rho_\sigma^0 V_\sigma f \frac{D_2 u_\sigma}{Dt} = \frac{PV_\sigma f}{\rho_\sigma^0} \frac{D_2 \rho_\sigma^0}{Dt} + f \eta \frac{2\Sigma}{a} + q_{1\sigma} + q_{2\sigma} - J_{1\sigma} (i_\sigma - i_1) - \rho_2^0 f \lambda (i_2 - i_\sigma) - J_{\sigma 1} f (i_1 - i_\sigma) - \rho_2^0 f \xi (i_\sigma - i_2). \quad (10)$$

The role of heat source or sink is taken by the  $\sigma$  phase. Here

$$\frac{d_1}{dt} = \frac{\partial}{\partial t} + v_1^h \nabla^h; \quad \frac{D_2}{Dt} = \frac{\partial}{\partial t} + v_2^h \nabla^h + \eta \frac{\partial}{\partial r}.$$

The hypothesis of local equilibrium within the limits of each phase is adopted, allowing the following relations to be written

$$\begin{aligned} \rho_1 \frac{d_1 s_1}{dt} &= \frac{\rho_1}{T_1} \frac{d_1 u_1}{dt} + \frac{\rho_1 P}{T_1} \frac{d_1 \left( \frac{1}{\rho_1^0} \right)}{dt} - \frac{\mu_{k1}}{T_1} \rho_1 \frac{d_1 c_{k1}}{dt} - \frac{\mu_{p1}}{T_1} \rho_1 \frac{d_1 c_{p1}}{dt}, \\ \rho_2^0 f r \frac{D_2 s_2}{Dt} &= \rho_2^0 \frac{f r}{T_2} \frac{D_2 u_2}{Dt} + \rho_2^0 \frac{f r P}{T_2} \frac{D_2 \left( \frac{1}{\rho_2^0} \right)}{Dt}, \\ \rho_\sigma^0 V_\sigma f \frac{D_2 s_\sigma}{Dt} &= \rho_\sigma^0 \frac{f V_\sigma}{T_\sigma} \frac{D_2 u_\sigma}{Dt} + \rho_\sigma^0 \frac{f V_\sigma P}{T_\sigma} \frac{D_2 \left( \frac{1}{\rho_\sigma^0} \right)}{Dt} \\ &- \frac{f \Sigma}{T_\sigma} \frac{d 4\pi a^2}{dt} - \frac{\mu_{k\sigma} \rho_\sigma^0 V_\sigma f}{T_\sigma} \frac{D_2 c_{k\sigma}}{Dt} - \frac{\mu_{p\sigma} \rho_\sigma^0 V_\sigma f}{T_\sigma} \frac{D_2 c_{p\sigma}}{Dt}, \\ i_1 - T_1 s_1 &= c_{k1} \mu_{k1} + c_{p1} \mu_{p1}, \quad i_\sigma - T_\sigma s_\sigma = c_{k\sigma} \mu_{k\sigma} + c_{p\sigma} \mu_{p\sigma}, \\ i_2 - T_2 s_2 &= \mu_2. \end{aligned} \quad (11)$$

Taking Eqs. (2), (5), and (8)-(11) into account, the substantial derivative of the mixture entropy is written in explicit form

$$\begin{aligned}
\rho \frac{DS}{Dt} = & -\frac{1}{T_1} \nabla q_1 + \frac{\rho_1 Q_1}{T_1} + \frac{1}{T_2} \int_0^R \rho_2^0 f r Q_2 dr + \\
& + \frac{1}{T_1} \int_0^R (\rho_2^0 r + \rho_\sigma^0 V_\sigma) f f_{12} (v_1 - v_2) dr + \int_0^R q_{1\sigma} \left( \frac{1}{T_\sigma} - \frac{1}{T_1} \right) dr + \\
& + \int_0^R q_{2\sigma} \left( \frac{1}{T_\sigma} - \frac{1}{T_2} \right) dr + \int_0^R J_{1\sigma} f \left\{ \left[ \frac{\mu_{h1}}{T_1} - \frac{\mu_{h\sigma}}{T_\sigma} \right] + i_1 \left[ \frac{1}{T_\sigma} - \frac{1}{T_1} \right] + \left[ -\frac{(v_2 - v_1)^2}{2 T_1} \right] \right\} dr + \\
& + \int_0^R J_{\sigma 1} f \left\{ \left[ \frac{\mu_{h\sigma}}{T_\sigma} - \frac{\mu_{h1}}{T_1} \right] + i_1 \left[ \frac{1}{T_1} - \frac{1}{T_\sigma} \right] + \left[ \frac{(v_2 - v_1)^2}{2 T_1} \right] \right\} dr + \int_0^R \rho_2^0 f \lambda \left\{ \left[ \frac{\mu_{h\sigma}}{T_\sigma} - \frac{\mu_{h2}}{T_2} \right] + \right. \\
& \left. + i_2 \left[ \frac{1}{T_2} - \frac{1}{T_\sigma} \right] \right\} dr + \int_0^R \rho_2^0 f \xi \left\{ \left[ \frac{\mu_{h2}}{T_2} - \frac{\mu_{h\sigma}}{T_\sigma} \right] + i_2 \left[ \frac{1}{T_\sigma} - \frac{1}{T_2} \right] \right\} dr.
\end{aligned} \tag{12}$$

The first three terms in Eq. (12) define the increment in mixture entropy (on account of influx of entropy from outside) due to energy transfer from the external medium, while the remaining seven define the increment in entropy on account of internal irreversible processes within and between phases: mechanical and thermal interactions between phases, phase transitions, and mass transfer.

## 2. Motive Forces of Crystallization

Each term in Eq. (12) is the product of a thermodynamic flux and the corresponding motive force. The motive forces associated with mass transfer may be enumerated as follows: for the mass transfer of material to the phase interface

$$X_{1\sigma} = \left[ \frac{\mu_{h1}}{T_1} - \frac{\mu_{h\sigma}}{T_\sigma} \right] + i_1 \left[ \frac{1}{T_\sigma} - \frac{1}{T_1} \right] + \left[ -\frac{(v_2 - v_1)^2}{2 T_1} \right], \tag{13}$$

for the crystallization process itself

$$X_{\sigma 2} = \left[ \frac{\mu_{h\sigma}}{T_\sigma} - \frac{\mu_{h2}}{T_2} \right] + i_2 \left[ \frac{1}{T_2} - \frac{1}{T_\sigma} \right], \tag{14}$$

for the mass transfer of material from the phase interface into the carrier

$$X_{\sigma 1} = \left[ \frac{\mu_{h\sigma}}{T_\sigma} - \frac{\mu_{h1}}{T_1} \right] + i_1 \left[ \frac{1}{T_1} - \frac{1}{T_\sigma} \right] + \left[ \frac{(v_2 - v_1)^2}{2 T_1} \right],$$

for the solution process itself

$$X_{2\sigma} = \left[ \frac{\mu_{h2}}{T_2} - \frac{\mu_{h\sigma}}{T_\sigma} \right] + i_2 \left[ \frac{1}{T_\sigma} - \frac{1}{T_2} \right].$$

The first term in the expression for the motive force of mass transfer from the carrier phase to the interface in Eq. (13) is due to the difference in chemical potential in the flow core and close to the crystal surface, the second to the thermal disequilibrium of the  $\sigma$  and carrier phases, and the third to the velocity disequilibrium.

The motive force of crystallization itself consists of two parts: the difference in Planck potentials  $\frac{\mu_{h\sigma}}{T_\sigma} - \frac{\mu_{h2}}{T_2}$

and an enthalpy motive force due to the thermal disequilibrium of the  $\sigma$  and  $r$ -th phases. There is no third term in Eq. (14), since velocity equilibrium is assumed between the  $r$ -th phase and the corresponding  $\sigma$  phase.

### 3. Crystal Growth Rate

Using linear Onsager relations (taking only the contribution of direct effects into account), the mass-transfer rate is determined

$$J_{1\sigma} = L_{1\sigma} \left\{ \left[ \frac{\mu_{h1}}{T_1} - \frac{\mu_{h\sigma}}{T_\sigma} \right] + i_1 \left[ \frac{1}{T_\sigma} - \frac{1}{T_1} \right] - \left[ \frac{(\mathbf{v}_2 - \mathbf{v}_1)^2}{2 T_1} \right] \right\}$$

and also the rate of crystallization itself

$$\rho_2^0 \lambda = L_{\sigma 2} \left\{ \left[ \frac{\mu_{h\sigma}}{T_\sigma} - \frac{\mu_{h2}}{T_2} \right] + i_2 \left[ \frac{1}{T_2} - \frac{1}{T_\sigma} \right] \right\}.$$

The chemical potentials  $\mu_{ki}$  are written in the form

$$\mu_{ki} = RT_i \ln \gamma_i + RT_i \left\{ \ln c_{hs}(T_2) + \frac{c_{hi} - c_{hs}(T_2)}{c_{hs}(T_2)} + \dots \right\}, \quad (15)$$

where  $L_{1\sigma}$  and  $L_{\sigma 2}$  are kinetic coefficients;  $\gamma_i$  is the activity coefficient of the component in the  $i$ -th phase; the subscript  $s$  corresponds to the state of saturation at temperature  $T_2$ .

Taking Eq. (15) into account, and omitting terms of second order of smallness and above (since the deviations from equilibrium are sufficiently small), the relations for the rates of mass transfer and phase transition are written in the form

$$J_{1\sigma} = L_{1\sigma} \frac{R}{c_s} \left\{ [c_1 - c_\sigma] + \frac{i_1 c_s}{R} \left[ \frac{1}{T_\sigma} - \frac{1}{T_1} \right] - \frac{c_s}{R} \frac{(\mathbf{v}_2 - \mathbf{v}_1)^2}{2 T_1} \right\}, \quad (16)$$

$$J_{\sigma 1} = L_{\sigma 1} \frac{R}{c_s} \left\{ [c_\sigma - c_1] + \frac{i_1 c_s}{R} \left[ \frac{1}{T_1} - \frac{1}{T_\sigma} \right] + \frac{c_s}{R} \frac{(\mathbf{v}_2 - \mathbf{v}_1)^2}{2 T_1} \right\}, \quad (17)$$

$$\rho_2^0 \lambda = L_{\sigma 2} \frac{R}{c_s} \{c_\sigma - c_s^*\}, \quad c_s^* = c_s \left[ 1 - \frac{i_2}{R} \left( \frac{1}{T_2} - \frac{1}{T_\sigma} \right) \right], \quad (18)$$

$$\rho_2^0 \xi = L_{2\sigma} \frac{R}{c_s} \{c_s^* - c_\sigma\}. \quad (19)$$

Temperature disequilibrium of the phases actually leads to change in the saturation concentration.

The kinetic coefficients  $L_{1\sigma}$  and  $L_{\sigma 2}$  will now be determined. At the crystal surface, there are adsorbed particles. Because of particle exchange between the step and adsorbed layer at the surface, particles are added to the crystal at fissures, and a value of the adsorbed-particle chemical potential close to  $\mu_2$  is established around the steps [2, 3]. The adsorbed particles undergo thermal oscillations in three directions: one perpendicular to the crystal surface and two parallel to it. Fluctuations of the first oscillations lead to breakaway of particles from the crystal surface and then to transition into the carrier phase; oscillations of the second type ensure diffusional migration of the particles along the crystal surface to the steps [2, 3]. Suppose that displacement of the elementary steps occurs on account of plane diffusion in one direction  $x$ . The flux of material to the steps may be written as  $D \frac{dc}{dx} dy dz$  where  $dz$  is the step height and  $dx = dy$  is assumed. The total flux of material to the steps at the crystal is obtained by summation

$$\sum_{i=1}^N D \frac{dc}{dx} dS_{S_i} \sim DS_S \frac{dc}{dx},$$

where  $N$  is the number of fissures over the entire surface of the crystal. On the other hand, this flux is also known to be

$$DS_S \frac{dc}{dx} \sim L_{\sigma 2} \frac{R}{c_s} (c_\sigma - c_s^*), \quad (20)$$

while  $D \sim d^2 \nu \exp(U_a/RT_2)$ .

Integrating Eq. (20) from 0 to  $d$ , the coefficient  $L_{\sigma 2}$  is determined

$$L_{\sigma_2} = DS_{\sigma} c_s' / (dR).$$

Hence, the crystal growth rate due to crystallization itself may be written as

$$\rho_2^0 \lambda = \frac{D}{d} S_{\sigma} (c_{\sigma} - c_s^*)$$

or

$$\rho_2^0 \lambda = \varepsilon \exp[-U_a/RT_2] S_{\sigma} [c_{\sigma} - c_s^*], \quad \varepsilon = \nu d. \quad (21)$$

The kinetic coefficient  $L_{1\sigma}$  is written in the form

$$L_{1\sigma} = \beta_M \frac{c_s}{R} S_{\sigma}.$$

#### 4. Verifying the Correctness of the Relations Obtained

To confirm the results obtained, experiments on the growth and solution of crystals being deposited in a vertical tube cell were performed, using two systems. A solution and crystals of aluminous alum were the first system chosen. The system of equations describing the motion and growth of the crystals, together with heat- and mass-transfer phenomena — a consequence of the system in Eqs. (1)–(10), (16), (17), and (21) — was solved for two values of the temperature (variant I:  $T_1 = 293^\circ\text{K}$ ,  $c_1 = 126 \text{ kg/m}^3$ ; variant II:  $T_1 = 295^\circ\text{K}$ ,  $c_1 = 126 \text{ kg/m}^3$ ) at different initial values of the crystal mass (0.5–1.2 mg). The kinetic coefficient  $\varepsilon$  and the parameter  $U_a$  in Eq. (21) were the unknowns. They were determined from a comparison of experimental and calculated data on the precipitation rate, by the method of scanning over a sufficiently broad range of values. For all the variants, the values obtained were the same ( $\varepsilon = 43.8 \text{ cm/sec}$ ;  $U_a = 13,250 \text{ J/mole}$ ; relative error 8%). The reason for these identical values is that the parameters  $\varepsilon$  and  $U_a$  are independent of the crystal mass. The coefficient  $\varepsilon \approx \nu d$ , where  $d \approx 10^{-8} \text{ cm}$  and  $\nu \in [10^7 - 10^{13} \text{ sec}^{-1}]$ , is equal to 43.8 cm/sec in the present case, i.e., lies in the given range. In the calculations for all the experiments it was found that: 1) the crystallization conditions are almost quasisteady; 2) the temperature at the crystal surface is higher than the temperature of the crystal itself by 0.005; 3) the temperature at the crystal surface is higher than the temperature of the solution by (0.06–0.1).

A solution and crystals of oxalic acid were chosen as the second system. Experiments were performed at temperatures in the range 303–323°K, at concentrations of 13–21%, and with different crystal masses (0.2–7 mg), with the aim of investigating the solution of oxalic-acid crystals in a cell-tube. The system of equations describing the motion and solution of the crystal, together with heat- and mass-transfer phenomena, is analogous to those for the first system. Earlier [4], the given system was investigated taking the supersaturation ( $c_1 - c_s$ ) as the motive force; solution occurred in the diffusional region, and the dependence  $\text{Nu} = \text{Ar}e^{0.52}$  was found for determining the mass-transfer coefficient  $\beta_M$ . In the present work, Eq. (17) was taken as the motive force. The mass-transfer coefficient was the unknown parameter. As a result of calculations for the system with crystals of different dimensions in different conditions, taking the relation for the motive force in Eq. (17) into account, the dependence  $\text{Nu} = \text{Ar}e^{0.52}$  was confirmed; the error in determining the rate of solution of the crystals according to the relation obtained was 7% lower than that determined in [4].

The contribution of the effects of the terms appearing in the dependence for the motive force of mass transfer in Eqs. (16) and (17) will now be estimated. If the contribution of the effect of the first term  $c_1 - c_{\sigma}$  is taken as 100%, then for the crystallization of aluminous alum the effect of the second term in Eq. (16) ( $(i_1 C_s / R)(1/T_1 - 1/T_{\sigma})$ ) is 3–30%; in the solution of oxalic acid crystals, the effect of the second term in Eq. (17) is from 0.1 to 4% and the effect of the third term in Eq. (17) is 10<sup>-4</sup>%. The contribution of the effect of the second term in the relation for the motive force of crystallization itself is 0.1–5% of the first term in Eq. (18).

Since the contribution of the enthalpic motive force is very significant, it might be expected that, in the case where the relations obtained were incorrect, the values of  $\varepsilon$  and  $U_a$  would be different for the growth of crystals of aluminous alum of different mass, and the temperature dependence of  $\beta_M$  in the solution of oxalic acid crystals would be stronger than the temperature dependence of the diffusion coefficient.

#### NOTATION

$r$ , crystal volume;  $V_{\sigma}$ , volume of  $\sigma$  phase;  $f(r)dr$ , number of crystals of dimension in the range ( $r - dr$ ,  $r + dr$ );  $\rho_1^0$ ,  $\rho_2^0$ ,  $\rho_{\sigma}^0$ , true density of carrier phase, crystal,  $\sigma$  phase, respectively;  $\lambda$ , rate of change of crystal volume due to crystallization itself;  $\xi$ , rate of change in crystal volume due to solution itself;  $\eta = \lambda - \xi$ , rate of change in

crystal volume;  $J_{1\sigma}f(r)dr$ , intensity of mass transfer from carrier phase to  $\sigma$  phase in unit volume per unit time;  $J_{\sigma 1}f(r)dr$ , intensity of mass transfer from  $\sigma$  phase into carrier phase;  $\rho_1$ , mean density of carrier phase,  $\rho_1 = \rho_1^0 \alpha_1$ ;  $\alpha_1$ , volume content of carrier phase,  $\alpha_1 + \int_0^R (r + V_{\sigma}) f(r) dr = 1$ ;  $R$ , volume of largest crystal;  $c_{ki}$ , concentration (mass fraction) of component in  $i$ -th phase;  $v_1, v_2(r)$ , velocity of carrier phase and particle of dimension (volume)  $r$ ;  $P$ , pressure;  $f_{12}$ , force of interaction between carrier phase and particle of dimension  $r$ , referred to particle mass;  $u_i$ , specific energy of  $i$ -th phase  $F_i$ , mass force acting on  $i$ -th phase;  $\Sigma$ , surface-tension coefficient;  $q_{i\sigma}$ , heat flux from the  $i$ -th phase to the  $\sigma$  phase;  $i_i$ , enthalpy of the  $i$ -th phase;  $T_i$ , temperature of the  $i$ -th phase;  $\mu_{ki}$ , chemical potential of the component in the  $i$ -th phase;  $\bar{\nabla}q_1$ , heat flux due to heat conduction in the first phase;  $Q_i$ , external heat flux in the  $i$ -th phase;  $S, s_i$ , specific entropy of the whole mixture and the  $i$ -th phase, respectively;  $J$ , flux of thermodynamic forces;  $X$ , thermodynamic force;  $R$ , universal gas constant;  $\gamma$ , activity coefficient;  $D$ , diffusion coefficient,  $L_{1\sigma}, L_{\sigma 1}, L_{2\sigma}, L_{\sigma 2}$ , kinetic coefficients;  $S_S$ , surface of the crystal;  $d$ , step height;  $\nu$ , oscillation frequency of atom;  $U_a$ , activation energy of transition between two neighboring equilibrium positions of the molecule at the surface;  $\beta_M$ , mass-transfer coefficient;  $c_S$ , equilibrium concentration at temperature  $T_2$ ;  $a$ , characteristic radius of particle;  $Nu = (\beta_M 2a)/D$ ;  $Re = (\rho_1^0 v_2 2a)/\mu_v$ ;  $\mu_v$ , viscosity coefficient of the solution;  $A$ , constant. Subscripts: 1, carrier phase; 2, disperse phase;  $\sigma$ ,  $\sigma$  phase;  $k$ , component;  $p$ , solvent;  $s$ , state of saturation;  $S$ , surface.

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#### ELEMENTARY KINETIC THEORY OF DIFFUSION IN GASES

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UDC 533.15

The results of research on the description of diffusion using the elementary kinetic theory are generalized. It is shown that for thermodiffusion and barodiffusion, this theory, bringing to light the physical essence of the phenomenon, leads to the same basic differential equations as the rigorous theory.

Introduction. The elementary kinetic theory first permitted expressing the transport coefficients (diffusion, viscosity, and thermal conductivity) in terms of the molecular characteristics of the gas. But, already with the description of the diffusion of a mixture of two gases, this theory encountered a number of difficulties. Boltzmann [1] obtained equations for the coefficients of diffusion of the separate components of binary mixtures, from which it followed that under isobaric-isothermic conditions each component has its own coefficient of diffusion, which leads to different flows of molecules in opposite directions. This should not occur with diffusion of gases in closed volumes (for example, in a pipe or in two volumes connected by capillaries). In this connection, Boltzmann assumed that the equations he obtained were not correct. Mayer [2] eliminated the contradiction by decreasing the flux of one type of molecule and increasing the flux of the other by an amount so that the two fluxes would equalize. The equations obtained by Mayer resulted in equal diffusion coefficients for components in a binary mixture, which is confirmed experimentally. However, Mayer's equation gave a strong concentration dependence of this coefficient, later called the coefficient of mutual diffusion, which is not observed experimentally. The strong concentration dependence of Mayer's diffusion coefficient was explained by the effect of homogeneous collisions of molecules. Maxwell [3], analyzing Loschmidt's experiments, already used an equation for the coefficient of mutual diffusion which did not contain a term that takes into account the effect of homogeneous collisions on the mean free path length. In all later theories, including also in the rigorous kinetic

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