A MATHEMATICAL MODEL OF THERMAL DIFFUSION IN WEAK SOLUTIONS OF ELECTROLYTES

M. T. Solodyak

We formulate a system of equations describing the interaction of electric, thermal, and diffusion processes in infinitely diluted solutions of electrolytes and investigate the process of electrodiffusion in the case where the concentration of neutral salt is given on the boundary of the body.

We construct a mathematical model of thermal diffusion in infinitely diluted (weak) solutions. This model enables one to express the chemical potential of every component via known (measurable) physicomechanical characteristics of the material, electrochemical equivalents, stoichiometric coefficients, and the molar mass of the constituent components.

For the macroscopic description of the interaction between the processes of heat and electric conduction, diffusion, and electrolytic dissociation, we use the hypothesis of local thermodynamic equilibrium [1–4]. The relations of equilibrium thermodynamics are true for any arbitrarily chosen physically small element of the system. To describe the state of this element, we use the following conjugate thermodynamic variables: temperature T, specific entropy S, pressure P, specific volume V ($\rho = 1/V$ is the density of particles), chemical potentials μ_k, and concentrations

$$C_k = \frac{m_k}{m},$$

where m_k and

$$m = \sum_{k=1}^{4} m_k$$

are the mass of the kth component and the total mass of the system, respectively, and parameters of the process (thermodynamic heat $\bar{J}_Q$ and mass $\bar{J}_k$ flows). The subscripts $k = \overline{1,4}$ denote cations, anions, and particles of salt and water, respectively. By using the identities

$$\sum_{k=1}^{4} C_k = 1 \quad \text{and} \quad \sum_{k=1}^{4} \bar{J}_k = 0, \tag{1}$$

we exclude the concentration and diffusion flow of water from consideration. In this case, the function of state (the specific internal energy U) depends on the parameters S, V, and C_k, i.e., $U = U(S, V, C_k)$, and its increment can be found by using the Gibbs equation [5, 6]

$$dU = T\,dS - P\,dV + \sum_{k=1}^{3} \mu_k \, dC_k, \tag{2}$$

where

$$S = c_p\left(1 + \ln\frac{T}{T_q}\right) + \frac{R}{M_*}\left(1 - \ln\frac{P}{P_q}\right) - R\sum_{k=1}^{4}\frac{C_k}{M_k}\left(\ln a_k + \frac{M_{k*}}{M_k}C_k\right),$$

$$P = \rho RT\sum_{k=1}^{4}M_{k*}\left(\frac{C_k}{M_k}\right)^2, \qquad \mu_k = \mu'_k - \mu'_4 - RT\left(\frac{1}{M_k} - \frac{1}{M_4} - \frac{M_{k*}}{M_k^2}C_k - \frac{M_{4*}}{M_4^2}C_4\right),$$

$$\mu'_k = \frac{RT}{M_k}\ln a_k\frac{P}{P_q}\left(\frac{T_q}{T}\right)^{(5+i_k)/2}, \qquad k = \overline{1,4}, \tag{3}$$

and, in addition,

$$a_k = \frac{M_k}{M_{k*}}\left(\frac{M_*}{M_k}\right)^{(5+i_k)/2}, \qquad \frac{1}{M_{k*}} = \left(\frac{1}{\tilde{M}_k} - \frac{C_{0k}}{M_k}\right)\frac{\rho_0 T_0}{\rho T} + \frac{C_k}{M_k}, \qquad \frac{1}{M_*} = \sum_{k=1}^{4}\frac{C_k}{M_k},$$

$$\tilde{M}_k = \frac{M_{0*}^{(5+i_{0*})/2}}{M_k^{(3+i_k)/2}}\left(\frac{T_0}{\Lambda}\right)^{(i_{0*}-i_k)/2}, \qquad i_* = \frac{2M_*}{R}C_p - 5 = M_*\sum_{k=1}^{4}\frac{i_k C_k}{M_k},$$

$$T_q = \frac{\Lambda}{M_*}, \qquad P_q = \frac{R\Lambda}{V_\mu M_*}, \qquad \Lambda = \frac{2\pi\hbar^2 N_A^2}{R}\left(\frac{N_A}{g_0 V_\mu}\right)^{2/3}, \tag{4}$$

μ_k is the relative chemical potential of the kth component (with respect to water), C_p is the heat capacity at constant pressure, M_* is the effective molar mass of the mixture, M_k is the molar mass of the kth component, i_k are additional degrees of freedom of the same component, R is the universal gas constant, V_μ is the volume of one mole of the ideal gas under normal conditions, N_A is the Avogadro number, $\hbar$ is the Planck constant, and g_0 is the statistic weight of an atom in the normal state depending on its orbital moment L and spin s. Here and in what follows, the subscript "0" denotes the quantities corresponding to the equilibrium state.

If we describe changes in the state of a system caused by the processes of electrodiffusion and electrolytic dissociation and by the action of electromagnetic fields, then, instead of the masses of cations and anions, one must use the spatially distributed electric charge Q and the degree of electrolytic dissociation Ξ as macroscopic parameters of state. By using the Faraday law [7, 8] and the de Donder principle [4], we can describe the indicated relationship by the formulas [6]

$$C_1 = k_1 Q + \nu_1\Xi, \qquad C_2 = k_2 Q + \nu_2\Xi, \qquad C_3 = C + \nu_3\Xi, \qquad \vec{J}_1 = k_1\vec{J}_q, \qquad \vec{J}_2 = k_2\vec{J}_q, \tag{5}$$

where k_1 and k_2 are the electrochemical equivalents of the cations and anions, ν_k is the bulk stoichiometric coefficient of the kth component $(k = \overline{1,3})$, and $\vec{J}_q$ is the conduction current density. Note that the stoichiometric coefficients satisfy the condition [4]

$$\nu_1 + \nu_2 + \nu_3 = 0, \tag{6}$$

which is a consequence of the law of conservation of mass in the course of chemical reactions. By virtue of relation (6), we can rewrite the normalizing condition (1) for parameters (5) as follows:

$$C + C_4 + (k_1 + k_2)Q = 1 \quad \text{and} \quad \vec{J} + \vec{J}_4 + (k_1 + k_2)\vec{J}_q = 0, \tag{7}$$

where $\vec{J}$ and $\vec{J}_4$ are the diffusion flows of salt and water.

We assume that, in the initial state, the system contains only water and neutral salt with concentrations C_{04} and C_0, respectively. Further, by using relations (5), we can write the expressions for the effective molar mass of the mixture in the equilibrium M_{0*} and nonequilibrium M_* states

$$\frac{1}{M_{0*}} = \frac{1}{M_4} + \frac{C_0}{M} \quad \text{and} \quad \frac{1}{M_*} = \frac{1}{M_4} + \frac{1}{M}(C + kQ + v\Xi) \tag{8}$$

and the effective molar masses of the components under consideration

$$\frac{1}{M_{i*}} = \frac{\rho_0 T_0}{\rho T \tilde{M}_i} + \frac{1}{M_i}(k_i Q + v_i \Xi), \quad i = \overline{1, 2},$$

$$\frac{1}{M_{3*}} = \frac{\rho_0 T_0}{\rho T}\left(\frac{1}{\tilde{M}_3} - \frac{C_0}{M_3}\right) + \frac{1}{M_3}(C + v_3 \Xi), \tag{9}$$

$$\frac{1}{M_{4*}} = \frac{\rho_0 T_0}{\rho T}\left(\frac{1}{\tilde{M}_4} - \frac{1 - C_0}{M_4}\right) + \frac{1}{M_4}(1 - C - (k_1 + k_2)Q).$$

Here, we assume that $C_{01} = C_{02} = 0$. In relations (8) and (9), we have used the following notation:

$$\frac{1}{M} = \frac{1}{M_3} - \frac{1}{M_4}, \quad k = M\left(\frac{k_1}{M_1} + \frac{k_2}{M_2} - \frac{k_1 + k_2}{M_4}\right), \quad \text{and} \quad v = M \sum_{i=1}^{3} \frac{v_i}{M_i}.$$

If we now substitute expressions (5) in Eq. (2), then we arrive at the fundamental equation of thermodynamics for infinitely diluted solutions:

$$dU = T dS - P dV + \mu dC + \varphi dQ + A d\Xi,$$

where $\mu = \mu_3$ is the relative chemical potential of salt, $\varphi = k_1 \mu_1 + k_2 \mu_2$ is the electrochemical potential, and

$$A = \sum_{k=1}^{3} v_k \mu_k$$

is the affinity of electrolytic dissociation.

By virtue of relations (3), (5), and (7), for chemical potentials, we obtain

$$\mu = RT(l_3 - l_4), \quad \varphi = RT[k_1 l_1 + k_2 l_2 - (k_1 + k_2)l_4], \quad A = RT \sum_{k=1}^{3} v_k l_k, \tag{10}$$

where

$$l_k = \frac{1}{M_k}\left[\ln a_k \frac{P}{P_k}\left(\frac{T_q}{T}\right)^{(5 + i_k)/2} - 1 + \frac{M_{k*}}{M_k} C_k\right], \quad k = \overline{1, 4},$$

and the quantities M_{k*} are given by relations (9).

We arrive at the following balance equations for the concentration of neutral salt C, the density of electric charge Q, and the degree of electrolytic dissociation Ξ [6]:

$$\rho \frac{dC}{dt} = -\vec{\nabla} \cdot \vec{J}, \quad \rho \frac{dQ}{dt} = -\vec{\nabla} \cdot \vec{J}_q, \quad \text{and} \quad \frac{d\Xi}{dt} = I, \tag{11}$$

where I is the rate of electrolytic dissociation per unit mass,

$$\frac{d}{dt} = \frac{\partial}{\partial t} + \vec{v} \cdot \vec{\nabla}$$

is the total time derivative,

$$\vec{\nabla} = \frac{\vec{i}^\alpha \partial}{\partial x^\alpha}$$

is the Hamiltonian operator, $\vec{i}^\alpha$ is a unit vector of the basis, x^α is a coordinate in the Cartesian coordinate system introduced in the Euler space, $\alpha = \overline{1, 3}$, and t is time. Here and in what follows, the dot placed between the variables denotes their convolution.

The equations of state (10) must be supplemented with the Maxwell equations

$$\vec{\nabla} \times \vec{H} = \frac{\partial \vec{D}}{\partial t} + \vec{j}, \quad \vec{\nabla} \times \vec{E} = \frac{\partial \vec{B}}{\partial t}, \quad \vec{\nabla} \cdot \vec{B} = 0, \quad \text{and} \quad \vec{\nabla} \cdot \vec{D} = \rho Q \tag{12}$$

and the following material relations used to express the vectors of electric $\vec{D}$ and magnetic $\vec{B}$ induction via the vectors of electric $\vec{E}$ and magnetic $\vec{H}$ field intensity:

$$\vec{D} = \varepsilon_0 \varepsilon \vec{E} + \frac{\varepsilon\mu - 1}{c^2} \vec{v} \times \vec{H} \quad \text{and} \quad \vec{B} = \mu_0 \mu \vec{H} - \frac{\varepsilon\mu - 1}{c^2} \vec{v} \times \vec{E}, \tag{13}$$

where $\vec{j} = \vec{J}_q + \rho Q \vec{v}$ is the density of the total electric current, ε_0 and μ_0 are the absolute electric and magnetic permittivities, and

$$c = \frac{1}{\sqrt{\varepsilon_0 \mu_0}}$$

is the velocity of light in vacuum.

By using the law of conservation of the total specific energy of the system [2] and the relations

$$\sum_{k=1}^{3} \mu_k \vec{J}_k = \mu_c \vec{J} + \varphi_q \vec{J}_q,$$

where

$$\mu_c = \mu + \frac{RT}{M_p} = \mu_3 - \mu_4 \quad \text{and} \quad \varphi_q = \varphi + k_p RT = k_1 \mu_1 + k_2 \mu_2 - (k_1 + k_2) \mu_4$$

are, respectively, the effective chemical and electrochemical potentials, and

$$\frac{1}{M_p} = \frac{1}{M} - \frac{M_{3*}}{M_3^2}(C + v_3\Xi) + \frac{M_{4*}}{M_4^2}C_4,$$

$$k_p = \frac{k}{M} - \left(\frac{k_1^2 M_{1*}}{M_1^2} + \frac{k_2^2 M_{2*}}{M_2^2}\right)Q - \left(\frac{k_1 v_1 M_{1*}}{M_1^2} + \frac{k_2 v_2 M_{2*}}{M_2^2}\right)\Xi + (k_1 + k_2)\frac{M_{4*}}{M_4^2}C_4,$$

we arrive at the equation of entropy balance in the form

$$\rho\frac{dS}{dt} = -\vec{\nabla}\cdot\vec{J}_s + T^{-1}\sigma_s. \tag{14}$$

The flow $\vec{J}_s$ and production σ_s of entropy are given by the formulas

$$\vec{J}_s = T^{-1}\vec{J}_Q, \qquad \sigma_s = \vec{J}_Q\cdot\vec{X}_Q + \vec{J}\cdot\vec{X}_c + \vec{J}_q\cdot\vec{X}_q + IX_A - P_\pi\vec{\nabla}\cdot\vec{v} - RT\left(\frac{1}{M_p}\vec{\nabla}\cdot\vec{J} + k_p\vec{\nabla}\cdot\vec{J}_q\right), \tag{15}$$

where

$$P_\pi = \rho RT \sum_{k=1}^{4} \frac{C_k}{M_k}\left(1 - \frac{M_{k*}}{M_k}C_k\right)$$

and, for the thermodynamical forces, we have

$$\vec{X}_Q = -T^{-1}\vec{\nabla}T, \qquad \vec{X}_c = -\vec{\nabla}\mu_c, \qquad \vec{X}_q = \vec{E} + \vec{v}\times\vec{B} - \vec{\nabla}\varphi_q, \quad \text{and} \quad X_A = -\rho A.$$

By using the principles of the theory of Onsager and Curie [1, 2, 4] and neglecting the cross effects, for infinitely diluted solutions, we obtain

$$\vec{J}_Q = -\frac{\kappa T_0}{T}\vec{\nabla}T, \qquad \vec{J} = -\lambda_c\vec{\nabla}\mu_c, \qquad \vec{J}_q = \lambda(\vec{E} + \vec{v}\times\vec{B} - \vec{\nabla}\varphi_q), \quad \text{and} \quad I = -\rho LA, \tag{16}$$

where κ and λ are, respectively, the coefficients of thermal and electric conductivity, λ_c is a quantity expressed via the diffusion coefficient, and L is the coefficient used to characterize the rate of the process of electrolytic dissociation. If we now substitute relations (16) in (11), then we can rewrite the balance equations for concentrations in the form

$$\rho\frac{dC}{dt} = \lambda_c\Delta\mu_c, \qquad \rho\frac{dQ}{dt} = -\lambda_c\vec{\nabla}\cdot(\vec{E} + \vec{v}\times\vec{B}) + \lambda\Delta\varphi_q, \quad \text{and} \quad \frac{d\Xi}{dt} = -\rho LA. \tag{17}$$

In view of relations (3), (15), and (16), Eq. (14) implies the following heat conduction equation:

$$\frac{1}{a}\frac{dT}{dt} = \frac{1}{T_0}\Delta\ln T + \frac{W}{\kappa}, \tag{18}$$

where

$$W = \sigma_s - \vec{J}_Q \cdot \vec{X}_Q - \rho RT \frac{d}{dt}\left[\frac{1}{M_*}\left(1 - \ln\frac{P}{P_q}\right) - \sum_{k=1}^{4}\frac{C_k}{M_k}\left(\ln a_k + \frac{M_{k*}}{M_k}C_k\right)\right] \qquad (19)$$

are heat sources and

$$a = \frac{\kappa}{\rho C_p}$$

is thermal diffusivity.

The equations of state (10) and electrodynamics (12) and (13), the balance equations (17) and (18), and the equations of conservation of the total mass and momentum [6] equipped with proper boundary and initial conditions (the model has twelve parameters) constitute a closed system of equations of thermal electrodiffusion in weak solutions of electrolytes. We consider two special cases.

Electrolytic Dissociation

Assume that the concentration C_0 of neutral salt in the body at the initial time is known and the diffusion flows are absent. Mathematically, this means that the original system of equations (12), (13), (17), and (18) has no operators depending on coordinates. In this approximation, there are only two equations for the functions Ξ and T, namely,

$$\frac{d\Xi}{dt} = -\rho LA, \qquad T\frac{dS}{dt} = \rho LA^2, \qquad A = RT\sum_{k=1}^{3}\nu_k l_k, \qquad S = C_p - R\sum_{k=1}^{4}C_k l_k, \qquad (20)$$

and

$$l_k = \frac{1}{M_k}\left[\ln\frac{\rho V_\mu}{M_{k*}}\left(\frac{\Lambda}{M_k T}\right)^{(3+i_k)/2} - 1 + \frac{M_{k*}}{M_k}C_k\right], \qquad k = \overline{1, 4},$$

$$\frac{1}{M_{i*}} = \frac{T_0}{T}\frac{1}{\tilde{M}_i} + \frac{\nu_i}{M_i}\Xi, \qquad i = 1, 2,$$

$$\frac{1}{M_{3*}} = \frac{T_0}{T}\left(\frac{1}{\tilde{M}_3} - \frac{C_0}{M_3}\right) + \frac{C_0 + \nu_3\Xi}{M_3}, \qquad \frac{1}{M_{4*}} = \frac{T_0}{T}\left(\frac{1}{\tilde{M}_4} - \frac{1-C_0}{M_4}\right) + \frac{1-C_0}{M_4},$$

where the concentrations of components (5) have the form $C_i = \nu_i \Xi$, $i = 1, 2$, $C_3 = C_0 + \nu_3 \Xi$, and $C_4 = 1 - C_0$.

For the static case $(t \to \infty)$, it follows from system (20) that $A = 0$. From the physical point of view, this means that the system is in the state of chemical equilibrium, i.e., the process of electrolytic dissociation is completed. In this case, the neutral salt is completely dissolved and we have $C_3 = 0$ and

$$\Xi = -\frac{C_0}{\nu_3}.$$

Moreover, by using the equation $A = 0$, one can determine the variation of temperature in the system.

Processes of Electrodiffusion for a Given Concentration of Neutral Salt on the Boundary of the Body

Let us now analyze the original system of equations of the model [Eqs. (10), (12), (13), (17), and (18)] for the case where the concentration of salt on the boundary of the body Σ

$$C_3(\vec{r}, t)|_\Sigma = C_0 \tag{21}$$

is fixed.

For infinitely dissolved solutions, we have $C_0 \ll 1$. This condition enables us to expand the twelve basic functions of the model in powers of their small deviations from the equilibrium state and linearize the problem. The *a priori* estimates established for this model show that, in the case under consideration (21), we can neglect the thermomechanical processes and reduce the problem to a system of four linear coupled differential equations for the concentration of salt C_3, the electric charge Q, the degree of electrolytic dissociation Ξ, and the electric field intensity $\vec{E}$ [6]:

$$\frac{\partial C}{\partial t} = D\Delta(C + k_c Q + v_c \Xi), \quad C = C_3 - v_3 \Xi, \quad \frac{\partial Q}{\partial t} = -\frac{1}{\tau_\varepsilon} Q + D_q \Delta \left(Q + \frac{C}{k_q} + \frac{v_q}{k_q} \Xi \right),$$

$$\frac{\partial \Xi}{\partial t} = -\frac{1}{\tau_\xi} \left(\Xi_0 + \Xi + \frac{C}{v_\xi} + \frac{k_\xi}{v_\xi} Q \right), \quad \vec{\nabla} \cdot \vec{E} = \frac{\rho}{\varepsilon\varepsilon_0} Q, \tag{22}$$

where we have used the following notation:

$$D = \frac{\lambda_c RT_0}{\rho M_4}\left(1 + \frac{M_4 \tilde{M}_3}{M_3^2}\right), \quad D_q = \frac{\lambda RT_0 k_q (k_1 + k_2)}{\rho M_4},$$

$$k_c = \frac{k_1 + k_2}{1 + M_4 \tilde{M}_3 M_3^{-2}}, \quad v_c = \frac{v_3}{1 + M_3^2 (M_4 \tilde{M}_3)^{-1}},$$

$$k_q = k_1 + k_2 + \frac{M_4}{k_1 + k_2}\left(\frac{\tilde{M}_1}{M_1^2} k_1^2 + \frac{\tilde{M}_2}{M_2^2} k_2^2\right), \quad v_q = \frac{M_4}{k_1 + k_2}\left(\frac{k_1 \tilde{M}_1}{M_1^2} v_1 + \frac{k_2 \tilde{M}_2}{M_2^2} v_2\right),$$

$$k_\xi = \frac{M_3^2}{v_3 \tilde{M}_3}\left(\frac{k_1 \tilde{M}_1}{M_1^2} v_1 + \frac{k_2 \tilde{M}_2}{M_2^2} v_2\right), \quad v_\xi = \frac{M_3^2}{v_3 \tilde{M}_3} \sum_{k=1}^{3} \frac{\tilde{M}_k}{M_k^2} v_k^2, \tag{23}$$

$$\tau_\varepsilon = \frac{\varepsilon\varepsilon_0}{\lambda}, \quad \tau_\xi = \frac{M_3^2}{\rho LRT_0 v_3^2 v_\xi \tilde{M}_3},$$

$$\Xi_0 = \frac{M_3^2 A_0}{RT_0 v_3 v_\xi \tilde{M}_3}, \quad A_0 = RT_0 \sum_{k=1}^{3} \frac{v_k}{M_k} \ln \frac{\rho V_\mu}{\tilde{M}_k}\left(\frac{\Lambda}{M_k T_0}\right)^{(3+i_k)/2},$$

D and D_q are the diffusion coefficients of neutral salt and electric charges, respectively, τ_ε is a characteristic electrodynamic time, and τ_ξ is a characteristic time of electrolytic dissociation. The remaining parameters in (23) characterize the coupled processes of diffusion of neutral and charged particles and the process of electrolytic dissociation.

In the process of electrolytic dissociation, the molar mass of cations and anions is always smaller than the molar mass of neutral salt, i.e., $M_i < M_3$ $(i = 1, 2)$. Therefore, relation (4) implies that $\tilde{M}_i \gg \tilde{M}_3$ and the analysis of relations (23) gives the following estimates:

$$\frac{v_c}{v} \ll 1 \quad \text{and} \quad \left(\frac{k_q}{k}, \frac{k_\xi}{k}, \frac{v_q}{v}, \frac{v_q}{v} \right) \gg 1. \tag{24}$$

By using these estimates, we can rewrite system (22) in the following simplified form:

$$\frac{\partial C}{\partial t} = D\Delta(C + k_c Q), \tag{25}$$

$$\frac{\partial Q}{\partial t} = -\frac{Q}{\tau_\varepsilon} + D_q \Delta\left(Q + \frac{\Xi v_q}{k_q} \right), \tag{26}$$

$$\frac{\partial \Xi}{\partial t} = -\frac{1}{\tau_\xi}\left(\Xi_0 + \Xi + \frac{Q k_\xi}{v_\xi} \right), \tag{27}$$

$$\vec{\nabla} \cdot \vec{E} = \frac{\rho Q}{\varepsilon \varepsilon_0}. \tag{28}$$

It is known [7] that the electrolytic dissociation of salts proceeds almost instantaneously, i.e., $\tau_\xi = 0$. This enables us to express the degree of electrolytic dissociation Ξ from Eq. (27) via the electric charge Q as follows:

$$\Xi = -\left(\Xi_0 + \frac{Q k_\xi}{v_\xi} \right). \tag{29}$$

Substituting this relation in formula (26), we arrive at the following equation for the electric charge:

$$\frac{\partial Q}{\partial t} = -\frac{Q}{\tau_\varepsilon} + D_q' \Delta Q, \tag{30}$$

where

$$D_q' = D\left(1 - \frac{v_q k_\xi}{v_\xi k_q} \right)$$

is the effective diffusion coefficient for electric charges.

Thus, we reduced the system of equations of electrodiffusion to a system of coupled equations for the concentration of neutral salt (25), electric charges (30), and electric filed intensity (28) and the algebraic relation (29) for the degree of electrolytic dissociation.

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