The electrode potential in modelling of transport processes in aqueous electrolytes

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In the paper equations of mathematical model of mechanical, heat, diffusion and electromagnetic processes in aqueous nonpolarized solutions of electrolyte with use of electrode potential are formulated. It is shown that under certain conditions new coupled parameters can be found: absolute temperature — entropy density, pressure — specific volume, chemical potential — concentration of anions, electrode potential — mass electric charge density. It enables to relate balance model equations with Maxwell equations.

Key words: heat conduction, diffusion, charged components, electromagnetic field.

Introduction. In many cases equations of mass and electric charge transport in liquid phase define fundamental properties of porous materials saturated with aqueous solution of electrolyte. The quantitative description of these processes is usually realized by continuous mechanics conceptions [1, 2] and methods of the non-equilibrium thermodynamics processes [3-5]. In the aim of include in equations of transport reciprocal reaction of charged molecules and electromagnetic field, the electrochemical potential [4, 6] or the electrode potential [7, 8] are use. We notice, that the electrode potential in description of influence of charged molecules distribution on mechanical behavior of metals was used in paper [9]. In case of using the electrochemical potential we get the set of equations of model of electrolyte, for which the formulation of chosen initial conditions is not trivial.

In present paper, in equations of transport processes we included the electrode potential [7] and equations for mechanical, heat, diffusion and electromagnetic in aqueous solutions of electrolyte without polarizations phenomena are formulated.

1. Gibb's equation and linear state equations

It assumed that the solution (electrolyte) consist of three components, which the fundamental component is a water molecule and two others (cations and anions) are charged molecules. In the macroscopic description each component of electrolyte correspond to continuum K_i ($i = 0, 1, 2$), and for total system — to continuum of mass centre K_c.

The mechanical, heat and electromagnetic processes are consider with use of kinematical characteristcs of continuum mass centre K_c, while diffusion processes as relative motion of continuum K_i points with respect to continuum K_c. The system occurs in the limited part of Euclidean space in Carthesian coordinates $\{x^\alpha\}$, where x^α are the coordinates ($\alpha = 1, 2, 3$).

Non-equilibrium processes in electrolyte will describe using local thermodynamical equilibrium hypothesis [3]. Let assume that, local state of the system is described by the coupled macroscopic parameters

$$T — s\,, \quad -P — v\,, \quad \mu'_k — C_k\,, \quad k = 0, 1, 2\,, \tag{1}$$

where T is the absolute temperature, s is the mass density of entropy, P is the pressure, v is the specific volume ($v = 1 / \rho$, $\rho = \sum \rho_k$ denotes the total density, ρ_k is the density of k-th component); μ'_k is the chemical potential k-th component of the system and $C_k = \rho_k / \rho$ its mass concentration.

Changes of parameters (1) are in agree with Gibbs and Euler equations, which with comply of condition of standarization of concentration ($\Sigma C_k = 1$) have a form [9, 10]

$$du = Tds - Pdv + \sum_{k=1}^{2} \mu_k dC_k\,, \quad u = Ts - Pv + \sum_{k=1}^{2} \mu_k dC_k + \mu'_0\,, \tag{2}$$

where u is the density of internal energy, $\mu_k = \mu'_k - \mu'_0$ is the specific chemical potential ($k = 1, 2$), μ'_0 is the chemical potential of water.

For description of diffusion of charged components and electromagnetic processes we introduce as independent parameter density of mass charge Ω_m, i. e.

$$\Omega_m = z_1 C_1 + z_2 C_2\,, \tag{3}$$

where $z_1 = z_1^* F / M_1$, $z_2 = z_2^* F / M_2$ are the mass densities of cations and anions charge of electrolyte, z_1^*, z_2^* are the valency numbers of cations and anions; M_1, M_2 are the atomic (molar) mass of cations and anions; $F = |e| \cdot N_A$ is the Faraday constant, $|e|$ is the absolute value of electron charge, N_A is the Avogadro number.

With comply of formula (3), Gibbs and Euler equations (2) have a form

$$du = Tds - Pdv + \mu_1^e dC_1 + \varphi d\Omega_m\,, \quad u = Ts - Pv + \mu_1^e C_1 + \varphi\Omega_m + \mu'_0\,, \tag{4}$$

where $\mu_1^e = \mu_1 - z\mu_2$ is the modified chemical potential ($z = z_1 / z_2$) and $\varphi = \mu_2 / z_2$ is the electrode potential [7].

We notice that similar form of equation (4) we get with using the electrochemical potential.

Use from a definition of density free Helmholtz energy, namely: $f = u - Ts - \varphi\Omega_m$, equations (4) rewrite in the following form

$$df = -sdT - Pdv + \mu_1^e dC_1 - \Omega_m d\varphi\,, \quad f = -Pv + \mu_1^e C_1 + \mu'_0\,. \tag{5}$$

In case, when free Helmholtz energy f is a thermodynamical potential, i. e. $f = f(T, v, C_1, \varphi)$, then from Gibbs equation (5) we get general form of state equations

$$s = -\left(\frac{\partial f}{\partial T}\right)_{v,C_1,\Omega_m} \; , \; P = -\left(\frac{\partial f}{\partial v}\right)_{T,C_1,\Omega_m} \; , \; \mu_1^e = \left(\frac{\partial f}{\partial C_1}\right)_{T,v,\Omega_m} \; , \; \Omega_m = -\left(\frac{\partial f}{\partial \varphi}\right)_{T,v,C_1} . \quad (6)$$

Accepted that free Helmholtz energy is an analitical function of independent parameters T, v, C_1, φ and assuming that in an initial equilibrium state, coupled parameters get values

$$T_0 \;—\; s_0, \;\; P_0 \;—\; v_0, \;\; \mu_{1(0)}^e \;—\; C_{1(0)}, \;\; \varphi_0 \;—\; \Omega_{m(0)}$$

and consider small deviation from this state

$$\delta T = T - T_0 \, , \quad \delta v = v - v_0 \, , \quad \delta C_1 = C_1 - C_{1(0)} \quad \delta \varphi = \varphi - \varphi_0 \, ,$$

we execute developments of free Helmholtz energy in Taylor series.

Then from state equations (6) we get following form of linear state equations

$$\delta s = c_v/T_0 \, \delta T - \alpha_T \delta v - d_{1T} \delta C_1 + d_{2T} \delta \varphi \, ,$$
$$\delta P = -\alpha_T \delta T - \alpha_v \delta v - d_{1v} \delta C_1 + d_{2v} \delta \varphi \, ,$$
$$\delta \mu_1^e = d_{1T} \delta T + d_{1v} \delta v + d_c \delta C_1 - d_{2c} \delta \varphi \, ,$$
$$\delta \Omega_m = d_{2T} \delta T + d_{2v} \delta v + d_{2c} \delta C_1 + d_\varphi \delta \varphi \, , \qquad (7)$$

where $\delta s = s - s_0$, $\delta P = P - P_0$, $\delta \mu_1^e = \mu_1^e - \mu_{1(0)}^e$ and $\delta \Omega_m = \Omega_m - \Omega_{m(0)}$ are the changes of coupled parameters;

$$c_v = T_0 \left(\frac{\partial^2 f}{\partial T^2}\right)_0 , \; \alpha_v = -\left(\frac{\partial P}{\partial v}\right)_0 , \; d_c = \left(\frac{\partial \mu_1^e}{\partial C_1}\right)_0 , \; d_\varphi = \left(\frac{\partial \Omega_m}{\partial \varphi}\right)_0 , \; \alpha_T = -\left(\frac{\partial P}{\partial T}\right)_0 ,$$

$$d_{1T} = \left(\frac{\partial \mu_1^e}{\partial T}\right)_0 , \; d_{2T} = \left(\frac{\partial \Omega_m}{\partial T}\right)_0 , \; d_{1v} = \left(\frac{\partial \mu_1^e}{\partial v}\right)_0 , \; d_{2v} = \left(\frac{\partial \Omega_m}{\partial v}\right)_0 , \; d_{2c} = \left(\frac{\partial \Omega_m}{\partial C_1}\right)_0$$

are physical constants.

2. Conservation and balance equations

Mass conservation equation. A differential form (local) of mass equation has a form

$$\frac{\partial \rho_k}{\partial \tau} + \vec{\nabla} \cdot (\rho_k \vec{\upsilon}_k) = 0 \, , \quad k = 0, 1, 2 \, , \qquad (8)$$

where $\vec{\upsilon}_k(\vec{r}, \tau)$ are the molecule velocity of k-th component of system (velocities of continuum points K_k), $\vec{\nabla} = \vec{i}^{\,\alpha} \, \partial/\partial x^\alpha$ is the Hamiltonian operator $\vec{i}^{\,\alpha}$ are the contravariant base vectors of the Carthesian coordinates ($\alpha = 1, 2, 3$), τ is the time.

The rule of total mass conservation of the system we get from equations (8) through their adding up

$$\frac{\partial \rho}{\partial \tau} = -\vec{\nabla} \cdot (\rho \vec{\upsilon}) = 0 \dots \text{ or } \dots \frac{1}{\rho}\frac{d\rho}{d\tau} = -\vec{\nabla} \cdot \vec{\upsilon},$$ (9)

where $\vec{\upsilon} = \rho^{-1} \sum_k \rho_k \vec{\upsilon}_k$ is the velocity of points of continuum mass centre K_c, $d/dt =$

$= \partial/\partial \tau + \vec{\upsilon} \cdot \vec{\nabla}$ is the full derivative (substantial derivative).

Equations of mass conservation of respective components (8) we can express in the form including mass concentrations of components

$$\rho \frac{dC_k}{d\tau} + \vec{\nabla} \cdot \vec{J}_k = 0, \quad k = 0, 1, 2,$$ (10)

where $\vec{J}_k = \rho_k (\vec{\upsilon}_k - \vec{\upsilon})$ is the diffusion flux.

Equations of charge balance. The rule of electric charge conservation we get from equations (10) by multiple of them by mass densities of charges z_k ($k = 1, 2$) and by their addition

$$\rho \frac{d\Omega_m}{d\tau} = -\vec{\nabla} \cdot \vec{j},$$ (11)

where $\vec{j} = \sum_{k=1}^{2} z_k \vec{J}_k$ is the density of conduction flux connected with ions diffusion.

The elecromagnetic field in the system and environment is determine from Maxwell's equations [4, 7]

$$\vec{\nabla} \times \vec{H} = \varepsilon_0 \varepsilon \frac{\partial \vec{E}}{\partial \tau} + \vec{I}, \quad \vec{\nabla} \times \vec{E} = -\mu_0 \mu \frac{\partial \vec{H}}{\partial \tau}, \quad \vec{\nabla} \cdot \vec{H} = 0, \quad \varepsilon \varepsilon_0 \vec{\nabla} \cdot \vec{E} = \Omega,$$ (12)

$$\vec{\nabla} \times \vec{H}_e = \varepsilon_0 \frac{\partial \vec{E}_e}{\partial \tau} + \vec{j}_e, \quad \vec{\nabla} \times \vec{E}_e = -\mu_0 \frac{\partial \vec{H}_e}{\partial \tau}, \quad \vec{\nabla} \cdot \vec{H}_e = 0, \quad \varepsilon_0 \vec{\nabla} \cdot \vec{E} = \Omega_e.$$ (13)

In equations (12) and (13) $\vec{E}, \vec{E}_e$ are intensities of electric field and $\vec{H}, \vec{H}_e$ are intensities of magnetic field in the system and environment; ε, μ are the electric and magnetic permittivities of electrolyte; ε_0, μ_0 are the electric and magnetic permittivities of vacuum; $\vec{I} = \Omega \vec{\upsilon} + \vec{j}$ is the density of electric flux in the system, where $\Omega = \rho \Omega_m$ and Ω_e is the density of the volume charge in the system and environment; $\vec{j}_e$ is the density of conduction flux in environment. The quantities Ω_e and $\vec{j}_e$ are in agree with a condition $\partial \Omega_e / \partial \tau = -\vec{\nabla} \cdot \vec{j}_e$.

When the equation for anions concentration C_2 replace by the equation of charge conservation, then the system of equations of model consist of differential equations: total mass conservation ρ, cations concentration C_1 and mass charge Ω_m, namely

$$\frac{d\rho}{d\tau} = -\rho\vec{\nabla}\cdot\vec{\upsilon}, \quad \rho\frac{dC_1}{d\tau} = -\vec{\nabla}\cdot\vec{J}_1, \quad \rho\frac{d\Omega_m}{d\tau} = -\vec{\nabla}\cdot\vec{j}. \tag{14}$$

Remaining qualities we define on the base of algebraical relationships

$$C_0 = 1 - \frac{1}{z_2}\Omega_m + (z-1)C_1, \quad C_2 = \frac{1}{z_2}\Omega_m - zC_1,$$

$$\vec{J}_2 = \frac{1}{z_2}\vec{j} - z\vec{J}_1, \quad \vec{J}_0 = -\frac{1}{z_2}\vec{j} + (z-1)\vec{J}_1, \quad z = \frac{z_1}{z_2}, \tag{15}$$

which are the result of using standarization conditions $\sum C_k = 1$ and $\sum \vec{J}_k = 0$ ($k = 0, 1, 2$) and definition of density of mass charge (3).

Equations of motion. The differential form of equation of motion for the total system is

$$\rho\frac{d\vec{\upsilon}}{d\tau} = \vec{\nabla}\cdot\hat{\sigma} + \vec{F} + \vec{F}_L, \tag{16}$$

where $\hat{\sigma}$ is the Cauchy's stress tensor [1], $\vec{F}$ and $\vec{F}_L$ is the mass force and the force related to the Lorentz force, with recpect to elementary volume.

Cauchy's stress tensor $\hat{\sigma}$ is related to tensor of pressure $\hat{P}$ by relation $\hat{\sigma} = -\hat{P}$ [2]. In the general case, tensor of pressure $\hat{P}$ is expressed by $\hat{P} = P\hat{I} + \hat{P}^{\upsilon}$, where P is the pressure in equilibrium, $\hat{P}^{\upsilon}$ is the tensor of viscous pressure. Tensor of viscous pressure $\hat{P}^{\upsilon}$ in the turn we write in form $\hat{P}^{\upsilon} = P^{\upsilon}\hat{I} + \hat{P}^{\upsilon a} + \hat{P}^{\upsilon s}$, where $P^{\upsilon} = \left(P_{11}^{\upsilon} + P_{22}^{\upsilon} + P_{33}^{\upsilon}\right)/3$ is the viscous pressure, $\hat{P}^{\upsilon a}, \hat{P}^{\upsilon s}$ are the antisymmetric and symmetric part of the deviator of tensor of viscous pressure $\hat{P}^{\upsilon}$.

The mass force is defined as $\vec{F} = \sum \rho_k \vec{F}_k'$, in which $\vec{F}_k'$ is the mass potential force ($\vec{F}_k' = -\vec{\nabla}\psi_k'$) which is conservative force ($\partial\psi_k'/\partial\tau = 0$), ψ_k' are potentials ($k = 0, 1, 2$).

The force $\vec{F}_L = \sum \rho_k \vec{F}_{L(k)}$ related to the Lorentz force $\vec{F}_{L(k)} = z_k\left(\vec{E} + \mu_0\vec{\upsilon}_k \times \vec{H}\right)$ acting on *k*-th element of the system, using density of eletrical flux and conduction flux, we write as follows $\vec{F}_L = \rho\Omega_m\vec{E} + \mu_0\vec{I} \times \vec{H}$.

We notice that, to get a form of equation of motion in agree with literature [2] we should to accept following relationships

$$P^{\upsilon} = \left(\frac{2}{3}\eta - \eta_{\upsilon}\right)\vec{\nabla}\cdot\vec{\upsilon}, \quad \hat{P}^{\upsilon s} = -2\eta\left(\vec{\nabla}\otimes\vec{\upsilon}\right)^s, \quad \hat{P}^{\upsilon a} = 0, \tag{17}$$

where η, η_{υ} are the form and volume viscosities respectively, $\left(\vec{\nabla}\otimes\vec{\upsilon}\right)^s$ is the symmetrical part of the dyad $\vec{\nabla}\otimes\vec{\upsilon}$.

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Equations of balance of potential, kinetic and electromagnetic energy. The balance equation of potential energy in total $\rho\psi = \sum\rho_k\psi_k$ $(k = 0, 1, 2)$ we get from the rule of mass conservation (8) elements of the system. In this aim, equation (8) we multiply by potential ψ'_k and summarize by all k. Take into account conditions of standarization we note

$$\rho\frac{d\psi}{d\tau} = -\vec{\nabla}\cdot\left(\sum_{k=1}^{2}\vec{J}_k\psi_k\right) - \upsilon\cdot\sum_{k=0}^{2}\rho_k\vec{F}'_k - \sum_{k=1}^{2}\vec{J}_k\cdot\vec{F}_k, \tag{18}$$

where $\psi_k = \psi'_k - \psi'_0$ is the relative mass potential, $\vec{F}_k = -\vec{\nabla}\psi_k$ $(k = 1, 2)$.

Equation of balance of kinetic energy we get from equation of balance of momentum (16) by scalar multiple with velocity vector $\vec{\upsilon}$ and take into account, that $\hat{\sigma} = -\hat{P}$, $\vec{F} = \sum_{k=0}^{2}\rho_k\vec{F}'_k$ and $\vec{F}_L = \rho\Omega_m\vec{E} + \mu_0\vec{I}\times\vec{H}$. Then we have

$$\rho\frac{d}{d\tau}\left(\frac{\upsilon^2}{2}\right) = -\vec{\nabla}\cdot\left(\vec{\upsilon}\cdot\hat{P}\right) + \hat{P}:\vec{\nabla}\otimes\vec{\upsilon} + \vec{\upsilon}\cdot\sum_{k=0}^{2}\rho_k\vec{F}'_k + \vec{\upsilon}\cdot\left(\rho\Omega_m\vec{E} + \mu_0\vec{I}\times\vec{H}\right). \tag{19}$$

Equations of balance of electromagnetic energy we get from Maxwell'equations

$$\frac{\partial}{\partial\tau}\left[\frac{1}{2}\left(\varepsilon\varepsilon_0 E^2 + \mu\mu_0 H^2\right)\right] = -\vec{\nabla}\cdot\left(\vec{E}\times\vec{H}\right) - \vec{E}\cdot\vec{I}. \tag{20}$$

The rule of energy conservation and equation of balance of internal energy. Density of total energy e with recpect to elementary volume of the system we define as follows

$$\rho e = \frac{1}{2}\left(\varepsilon\varepsilon_0 E^2 + \mu\mu_0 H^2\right) + \rho\left(\frac{\vec{\upsilon}^2}{2} + \psi + u\right). \tag{21}$$

When the density of flux of total energy we assume in the form

$$\vec{J}_e = \rho\left(\frac{\vec{\upsilon}^2}{2} + \psi + u\right)\vec{\upsilon} + \vec{E}\times\vec{H} + \hat{P}\cdot\vec{\upsilon} + \sum_{k=1}^{2}\left(\mu_k + \psi_k\right)\vec{J}_k + \vec{J}_Q, \tag{22}$$

where $\vec{J}_Q$ is the flux of heat, then the rule of conservation of total energy has a form

$$\frac{\partial(\rho e)}{\partial\tau} = -\vec{\nabla}\cdot\vec{J}_e. \tag{23}$$

Equations of balance of internal energy we get, when we substitute expression (21) and (22) to equation (23) and we use equation of balance of potential energy (18), kinetic (19) and electromagnetic energy (20). Using equations (14) we notice them in a form

$$\rho\frac{du}{d\tau} = -\vec{\nabla}\cdot\vec{J}_Q + \frac{P}{\rho}\frac{d\rho}{d\tau} + \mu_1^e\rho\frac{dC_1}{d\tau} + \varphi\rho\frac{d\Omega_m}{d\tau} +$$

$$+\vec{J}_1 \cdot \vec{X}_1 + \vec{j} \cdot \vec{X}^e + P^\upsilon X_\upsilon + \hat{P}^{\upsilon s} : \hat{X}^{\upsilon s} + \hat{P}^{\upsilon a} : \hat{X}^{\upsilon a}, \tag{24}$$

where $\vec{X}_1 = -\vec{\nabla}\left(\mu_1^e + \psi_1^e\right), \vec{X}^e = -\vec{\nabla}\left(\varphi + \varphi_e + \psi_2^e\right) + \mu_0 \vec{\upsilon} \times \vec{H}, X_\upsilon = -\vec{\nabla}\cdot\vec{\upsilon}, \hat{X}^{\upsilon s} = -\left(\vec{\nabla}\otimes\vec{\upsilon}\right)^s$

and $\hat{X}^{\upsilon a} = -\left(\vec{\nabla}\otimes\vec{\upsilon}\right)^a$ are the thermodynamic forces coupled to density of flux of cations $\vec{J}_1$, flux od conduction $\vec{j}$, viscous pressure, symmetric part of tensor of viscous pressure $\hat{P}^{\upsilon s}$ and antisymmetric part of pressure tensor $\hat{P}^{\upsilon a}$; $\left(\vec{\nabla}\otimes\vec{\upsilon}\right)^a$ is the antisymmetrical part of the deviator of tensor $\vec{\nabla}\otimes\vec{\upsilon}$; $\psi_1^e = \psi_1 - z\psi_2$, $\psi_2^e = \psi_2/z_2$ are the transformed potentials of mass forces, φ_e is the electric potential $\left(\vec{E} = -\vec{\nabla}\varphi_e\right)$.

3. Equation of balance of entropy and kinetic equations

Let consider boundary transition to equilibrium changes in the system. In this case we reduce all fluxes to null, i. e. $\vec{J}_Q \to 0$, $\vec{J}_1 \to 0$, $\vec{j} \to 0$ and $\hat{P}^\upsilon \to 0$. Except this, we involve definition of entropy [10, 11]. From definition of entropy and heat flux $\vec{J}_Q$ we have

$$\lim_{\vec{J}_Q \to 0}\left(\vec{\nabla}\cdot\vec{J}_Q\right) = -\rho T \frac{ds}{d\tau}. \tag{25}$$

Then from equation of balance of internal energy (24) we get

$$\rho\frac{du}{d\tau} = \rho T \frac{ds}{d\tau} + \frac{P}{\rho}\frac{d\rho}{d\tau} + \mu_1^e\rho\frac{dC_1}{d\tau} + \varphi\rho\frac{d\Omega_m}{d\tau}. \tag{26}$$

The change of state of the system and following physical quantities u, s, ρ, C_1 and Ω_m for this case runs quasi-static.

Equation of balance of entropy we lead out by comparison of equation of balance of internal energy (24) for real and quasi-static processes (26). In further part we neglect the influence of mass forces ($\psi_1^e = 0$, $\psi_2^e = 0$), volumetric and rotating viscosity ($P^\upsilon = 0$, $\hat{P}^{\upsilon a} = 0$), then we have

$$\rho\frac{ds}{d\tau} = -\vec{\nabla}\cdot\vec{J}_s + \frac{1}{T}\left(\vec{J}_Q\vec{X}_Q + \vec{J}_1\cdot\vec{X}_1 + \vec{j}\cdot\vec{X}^e + \hat{P}^{\upsilon s}:\hat{X}^{\upsilon s}\right), \tag{27}$$

where $\vec{J}_s = \vec{J}_Q/T$ is the flux of entropy, $\vec{X}_Q = -\vec{\nabla}T/T$ is the thermodynamic force coupled to density of flux of heat $\vec{J}_Q$,

Kinetic equations. Let assume that fluxes are function of forces. For isotropic media are associated only fluxes and forces equal tensor nature [4], this means

$$\vec{J}_Q = \vec{J}_Q\left(\vec{X}_Q, \vec{X}_1, \vec{X}^e\right), \quad \vec{J}_1 = \vec{J}_1\left(\vec{X}_Q, \vec{X}_1, \vec{X}^e\right),$$
$$\vec{j} = \vec{j}\left(\vec{X}_Q, \vec{X}_1, \vec{X}^e\right), \quad \hat{P}^{\upsilon s} = \hat{P}^{\upsilon s}\left(\hat{X}^{\upsilon s}\right). \tag{28}$$

For homogeneous system in equilibrium, forces and thermodynamic fluxes are equal null, then for small deviations from equilibrium positions we can assume linear relationship between fluxes and forces in a form

$$\vec{J}_Q = L_{QQ}\vec{X}_Q + L_{Q1}\vec{X}_1 + L_{Qe}\vec{X}^e , \qquad \vec{J}_1 = L_{1Q}\vec{X}_Q + L_{11}\vec{X}_1 + L_{1e}\vec{X}^e , \tag{29}$$

$$\vec{j} = L_{eQ}\vec{X}_Q + L_{e1}\vec{X}_1 + L_{ee}\vec{X}^e , \qquad \hat{P}^{\upsilon s} = \hat{\hat{L}} : \hat{X}^{\upsilon s} \tag{30}$$

where L_{QQ}, L_{Q1}, L_{Qe}, L_{1Q}, L_{11}, L_{1e}, L_{eQ}, L_{e1}, L_{ee} are the scalar kinematics coefficients and $\hat{\hat{L}}$ is the tensor's kinematic coefficient (isotropic tensor of 4-th order).

We mark, that these coefficients should be well-chosen to comply the second thermodynamic principle and equalities $L_{Q1} = L_{1Q}$, $L_{Qe} = L_{eQ}$, $L_{1e} = L_{e1}$, which are the result of Onsager principle [2, 4].

4. Key equations

Using the linear state equations (7) for the modified chemical potential μ_1^e, assuming that, characteristics of material d_{1T}, d_{1v}, d_c and d_{2c} are constants, expressions for thermodynamic force $\vec{X}_1$ we write in a form

$$\vec{X}_1 = -d_{1T}\vec{\nabla}T - d_{1v}\vec{\nabla}v - d_c\vec{\nabla}C_1 - d_{2c}\vec{\nabla}\varphi . \tag{31}$$

The form others thermodynamical forces stay without changes.
Substitutting expressions of thermodynamical forces in kinetic equations (29) we get

$$\vec{J}_Q = -\bar{\chi}\vec{\nabla}T - \bar{\chi}_v\vec{\nabla}v - \bar{\chi}_c\vec{\nabla}C_1 - \bar{\chi}_\varphi\vec{\nabla}\varphi - L_{Qe}\left(\vec{\nabla}\varphi_e - \mu_0\vec{\upsilon}\times\vec{H}\right),$$

$$\vec{J}_1 = -\bar{D}_T\vec{\nabla}T - \bar{D}_v\vec{\nabla}v - \bar{D}_c\vec{\nabla}C_1 - \bar{D}_\varphi\vec{\nabla}\varphi - L_{1e}\left(\vec{\nabla}\varphi_e - \mu_0\vec{\upsilon}\times\vec{H}\right),$$

$$\vec{j} = -\bar{\Lambda}_T\vec{\nabla}T - \bar{\Lambda}_v\vec{\nabla}v - \bar{\Lambda}_c\vec{\nabla}C_1 - \bar{\Lambda}_\varphi\vec{\nabla}\varphi - L_{ee}\left(\vec{\nabla}\varphi_e - \mu_0\vec{\upsilon}\times\vec{H}\right),$$

$$\hat{P}^{\upsilon s} = -\hat{\hat{L}} : \left(\vec{\nabla}\otimes\vec{\upsilon}\right)^s , \tag{32}$$

where quantities marked by line refer to the modified material constants.
Equation of heat conduction we obtain from equation of balance of entropy (27)

$$\frac{c_v}{T_0}\rho\frac{dT}{d\tau} - \alpha_T\rho\frac{dv}{d\tau} + d_{1T}\rho\frac{dC_1}{d\tau} + d_{2T}\rho\frac{d\varphi}{d\tau} =$$

$$= \vec{\nabla}\cdot\left(\chi\vec{\nabla}T + \chi_v\vec{\nabla}v + \chi_c\vec{\nabla}C_1 + \chi_\varphi\vec{\nabla}\varphi + \bar{L}_{Qe}\vec{\nabla}\varphi_e - \bar{L}_{Qe}\mu_0\vec{\upsilon}\times\vec{H}\right) + Q_n , \tag{33}$$

where $\chi = \bar{\chi}/T$, $\chi_v = \bar{\chi}_v/T$, $\chi_c = \bar{\chi}_c/T$, $\chi_\varphi = \bar{\chi}_\varphi/T$, $\bar{L}_{Qe} = L_{Qe}/T$ and $Q_n = \sigma_s\left(\vec{\nabla}T, \vec{\nabla}v, \vec{\nabla}C_1, \vec{\nabla}\varphi, ...\right)$ is non-compensated heat [10].

Equation of diffusion of cations we obtain by substittuting to equation of concentration balance (14) right expressions for flux (32). Then

$$\rho \frac{dC_1}{d\tau} = \vec{\nabla} \cdot \left(\bar{D}_T \vec{\nabla} T + \bar{D}_v \vec{\nabla} v + \bar{D}_c \vec{\nabla} C_1 + \bar{D}_\varphi \vec{\nabla} \varphi + L_{1e} \vec{\nabla} \varphi_e - L_{1e} \mu_0 \vec{\upsilon} \times \vec{H} \right). \qquad (34)$$

Equation of diffusion of electric charge we obtain from the balance equation of charge (14) and expression for conduction flux $\vec{j}$ from (32). We have

$$\rho \frac{d\Omega_m}{d\tau} = \vec{\nabla} \cdot \left(\bar{\Lambda}_T \vec{\nabla} T + \bar{\Lambda}_v \vec{\nabla} v + \bar{\Lambda}_c \vec{\nabla} C_1 + \bar{\Lambda}_\varphi \vec{\nabla} \varphi + L_{ee} \vec{\nabla} \varphi_e - L_{ee} \mu_0 \vec{\upsilon} \times \vec{H} \right). \qquad (35)$$

Take into account chosen simplifications from equation of motion (16), we get

$$\rho \frac{d\vec{\upsilon}}{d\tau} = -\vec{\nabla} P + \vec{\nabla} \cdot \left[\hat{\hat{L}} : \left(\vec{\nabla} \otimes \vec{\upsilon} \right)^s \right] + \vec{F}_L. \qquad (36)$$

Underline that, in this case should be take into account equations of balance of total mass (14) and Maxwell equations (12), in which quantities $\vec{I}$ i Ω are determined with regard to state equations (7) for charge Ω_m and kinetic relation (32) for flux of density of conduction flux $\vec{j}$.

5. Linearized key equations

After neglecting geometrical non-linearity related to convection motion of the system points ($d/d\tau \cong \partial/\partial\tau$) and neglecting adiabatic relationship of thermodynamical processes ($\rho \, ds/d\tau \cong \left(c_v \rho / T_0 \right) dT/d\tau$), assuming constant density of the system ($\rho \cong \rho_0$) and its material characteristics, and also $\hat{\hat{L}} = 2\eta \hat{I} \otimes \hat{I}$, we have

$$\frac{c_v}{T_0} \rho_0 \frac{\partial T}{\partial \tau} = \chi \Delta T + \chi_c \Delta C_1 + \chi_\varphi \Delta \varphi + L_{Qe} \Delta \varphi_e - L_{Qe} \mu_0 \vec{\nabla} \cdot \left(\vec{\upsilon} \times \vec{H} \right) + Q_n, \qquad (37)$$

$$\frac{\partial C_1}{\partial \tau} = D_T \Delta T + D_c \Delta C_1 + D_\varphi \Delta \varphi + L'_{1e} \Delta \varphi_e - L'_{1e} \mu_0 \vec{\nabla} \cdot \left(\vec{\upsilon} \times \vec{H} \right). \qquad (38)$$

$$\frac{\partial \Omega_m}{\partial \tau} = \Lambda_T \Delta T + \Lambda_c \Delta C_1 + \Lambda_\varphi \Delta \varphi + L'_{ee} \Delta \varphi_e - L'_{ee} \mu_0 \vec{\nabla} \cdot \left(\vec{\upsilon} \times \vec{H} \right). \qquad (39)$$

$$\vec{\nabla} \cdot \vec{\upsilon} = 0, \qquad \frac{\partial \vec{\upsilon}}{\partial \tau} = -\frac{1}{\rho_0} \vec{\nabla} P + \frac{2\eta}{\rho_0} \vec{\nabla} \cdot \left(\vec{\nabla} \otimes \vec{\upsilon} \right)^s + \frac{1}{\rho_0} \vec{F}_L, \qquad (40)$$

$$\vec{\nabla} \times \vec{H} = \varepsilon_0 \varepsilon \frac{\partial \vec{E}}{\partial \tau} + \vec{I}, \qquad \vec{\nabla} \times \vec{E} = -\mu_0 \mu \frac{\partial \vec{H}}{\partial \tau}, \qquad \vec{\nabla} \cdot \vec{H} = 0, \qquad \varepsilon \varepsilon_0 \vec{\nabla} \cdot \vec{E} = \Omega, \qquad (41)$$

where quantities

$$\vec{F}_L = \rho \Omega_m \vec{E} + \mu_0 \left[\vec{I} \times \vec{H} \right], \qquad \vec{I} = \Omega \vec{\upsilon} + \vec{j}, \qquad \Omega = \rho \Omega_m$$

are expressed by demand function $T, C_1, \Omega_m, \vec{\upsilon}, P$ with use of kinetic equation

$$\vec{j} = -\rho_0 \left(\Lambda_T \vec{\nabla} T + \Lambda_c \vec{\nabla} C_1 + \Lambda_\varphi \vec{\nabla} \varphi \right) - L_{ee} \left(\vec{\nabla} \varphi_e - \mu_0 \vec{\upsilon} \times \vec{H} \right)$$

and state equations $\delta\Omega_m = d_{2T}\delta T + d_{2c}\delta C_1 + d_\varphi\delta\varphi$. Where $\chi = \overline{\chi}/\rho_0$, $\chi_\nu = \overline{\chi}_\nu/\rho_0$, $\chi_c = \overline{\chi}_c/\rho_0$, $\chi_\varphi = \overline{\chi}_\varphi/\rho_0$, $D_T = \overline{D}_T/\rho_0$, $D_\nu = \overline{D}_\nu/\rho_0$, $D_c = \overline{D}_c/\rho_0$, $D_\varphi = \overline{D}_\varphi/\rho_0$, $\Lambda_T = \overline{\Lambda}_T/\rho_0$, $\Lambda_\nu = \overline{\Lambda}_\nu/\rho_0$, $\Lambda_c = \overline{\Lambda}_c/\rho_0$, $\Lambda_\varphi = \overline{\Lambda}_\varphi/\rho_0$, $L'_{1e} = L_{1e}/\rho_0$, $L'_{ee} = L_{ee}/\rho_0$ are modiffied material constants.

6. Boundary conditions

We assume, that functions Ω_e and $\vec{j}_e$, decribing distribution of charge and electric fluxes in environment differ from null in limited part of space and on separate surface Γ are absent charge Ω_Γ and electric flux $\vec{i}$. For initial conditions we assume values of velocity, temperature, concentration, electric potential, and magnetic field in initial moment of time $\tau = 0$, which satisfy outgoing equilibrium state of the system. In this case

$$\vec{\upsilon} = 0, \quad P = 0, \quad C_1 = 0, \quad \varphi = 0, \quad \vec{E} = 0, \quad \vec{H} = 0, \quad \vec{E}_e = 0, \quad \vec{H}_e = 0. \quad (42)$$

If on separate surface with non-polarizeable and electrically non-conducting environment assigned external loading by the force $\vec{p}_e$, for forces in the system we give a condition

$$-\left(P\hat{I} + \hat{P}^{\upsilon s} \right) \cdot \vec{n} = \vec{p}_e. \quad (43)$$

For heat processes we assume conditions of first, second and third kind

$$T = T_\Gamma, \quad \frac{\partial T}{\partial n} = J_\Gamma, \quad \frac{\partial T}{\partial n} + h_0 (T - T_e) = J_e, \quad (44)$$

where T_Γ, T_e are temperatures on the system surface and environment; $\partial T/\partial n$ is directional derivative of temperature along the normal to medium surface; h_0 is the relative coefficient of energy in heat form; J_Γ, J_e are well-known functions of points of the system surface and time.

For the electrode potential φ and for vectors of electromagnetic field $\vec{E}$ and $\vec{H}$ we have

$$\varphi = -\Phi_0, \quad \vec{n} \times \left(\vec{H}_e - \vec{H} \right) = 0, \quad \vec{E}_{el} - \vec{E}_l = 0,$$
$$E_{en} - E_n = 0, \quad H_{en} - H_n = 0, \quad (45)$$

where Φ_0 is a value of electrode potential φ on the system surface; $\vec{E}_{el}$ and $\vec{E}_l$ are a projection right field vectors on contiguous plane to the system surface; E_{en}, E_n are normal components of electric field and H_{en}, H_n are normal components of magnetic field.

For diffusion process on surface Γ we assume

$$\mu_1^e = \mu_\Gamma \quad \text{or} \quad C_1 = C_\Gamma, \quad (46)$$

where μ_Γ and C_Γ are well-known functions. If surface of the system is mass-isolated, this fulfils a condition $\vec{J}_1 \cdot \vec{n} = 0$.

In similar way formulate contact conditions.

Conclusions. In present paper we formulated equations of mathematical model of mechanical, heat, diffusion and electromagnetic processes in aqueous solutions of electrolyte using the electrode potential without polarization phenomena.

In the quality of coupled parameters describing the local state of the system we chosen: absolute temperature — density of entropy, pressure — specific volume, chemical potential — concentrations of ions and electrode potential — mass density of electric charge. It enabled to connect in natural way balance equations of the model with Maxwell equations.

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Електродний потенціал у моделюванні процесів перенесення в електроліті

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У роботі отримано вихідні співвідношення математичної моделі механічних, теплових, дифузійних та електромагнітних процесів у водних неполяризовних розчинах електроліту з використанням електродного потенціалу. Параметрами локального стану розчину вибрано абсолютну температуру — масову густину ентропії, тиск — питомий об'єм, хімічні потенціали — концентрації компонент. Показано, що з використанням масової густини електричного заряду компонент (катіонів і аніонів) та умови нормування концентрацій, можна визначити нові спряжені параметри, а саме: узагальнений хімічний потенціал — концентрацію аніонів та електродний потенціал — масову густину електричного заряду середовища. Введення масової густини електричного заряду середовища у простір параметрів стану дозволяє визначити прямий зв'язок відповідних рівнянь стану та балансових співвідношень

із рівняннями Максвелла. Виходячи з потенціальності внутрішньої енергії (вільної енергії Гельмгольца), із сформульованих рівнянь Гіббса й Ейлера отримано лінійні рівняння стану. Закони збереження та балансові рівняння моделі записано для густини маси, концентрації аніонів, масової густини електричного заряду середовища, імпульсу й ентропії. З цих рівнянь, використовуючи кінетичні рівняння та рівняння стану, одержано розв'язуючу систему рівнянь моделі. Сформульовано відповідні початкові та граничні умови.

Электродный потенциал в моделировании процессов переноса в электролите

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В работе получены исходные соотношения математической модели механических, тепловых, диффузионных и электромагнитных процессов в водных растворах электролитов с использованием электродного потенциала без учета поляризации среды. В качестве параметров, характеризующих локальное состояние раствора, выбраны абсолютная температура — массовая плотность энтропии, давление — удельный объем, химические потенциалы — концентрации компонент. Показано, что, используя массовые плотности электрических зарядов компонент (катионов и анионов) и условия нормирования концентраций можно ввести новые сопряженные параметры: обобщенный химический потенциал — концентрацию анионов и электродный потенциал — массовую плотность электрического заряда среды. Использование в качества параметра состояния массовой плотности электрического заряда среды позволяет установить непосредственную связь соответствующих уравнений состояния и балансовых соотношений с уравнениями Максвелла. Исходя из потенциальности внутренней энергии (свободной энергии Гельмгольца) из сформулированных уравнений Гиббса и Эйлера получены линейные уравнения состояния. Законы сохранения и балансовые уравнения модели записаны для плотности массы, концентрации анионов, массовой плотности электрического заряда среды, импульса и энтропии. Из этих уравнений, используя кинетические уравнения и уравнения состояния, получена разрешающая система уравнений модели. Сформулированы соответствующие начальные и граничные условия.