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DIFFUSIONAL-ELECTRICAL PHENOMENA IN ELECTROLYTES

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For a macroscopic description of transfer processes it is suggested to use the equations of the thermodynamics of irreversible processes and the Poisson equation. With such an approach adopted, there is no necessity of introducing and determining the coefficients of molecular diffusion of cations and anions.

The medium under discussion is assumed to consist of a non-ionized solvent, an electrolyte in the form of ions and uncharged components. At first we consider infinitely diluted electrolytes when molecules are completely dissociated into cations and anions.

In a solution, ions are transferred by convection, diffusion, and migration in the presence of an electric field. Derivation of the equation for ion migration is based on the following considerations. In a solution with molar concentration n and diffusion coefficient D_i let there be ions with charge z_i. When an ion is exposed to an electric field with intensity E applied to the solution, the ion experiences the force z_ieE, which brings it into motion. The ion velocity is related to this force by the usual expression known for the motion of particles in a viscous medium:

$$u = \gamma_i^* z_i e E, \tag{1}$$

where γ_i^* is the ion mobility. The latter may be expressed in terms of the diffusion coefficient using the known Einstein relation:

$$\gamma_i^* = \frac{D_i F}{RT}. \tag{2}$$

The total flux of ions of the i-th kind in a moving medium in the presence of diffusion and migration is determined by the Nernst-Planck equation:

$$q_i = n_i v - D_i \nabla n_i + \frac{D_i z_i F E}{RT} n_i. \tag{3}$$

Formulas (1) and (2) have, in fact, a limited sphere of applicability. Indeed, A. Einstein's work [1] is concerned only with the diffusion of a neutral impurity with its small concentration in a solution when the usual relations of hydrodynamics are valid for a flow around a sphere.

In the physics of plasma, formulas (1) and (2) are based on other considerations and provided the plasma is weakly ionized, i.e., particles move independently of each other. Here, only the collision of charged particles with neutral ones is taken into account [2].

In [3, 4], for describing the diffusion and migration of ions in a partially dissociated electrolyte it is suggested to take into consideration their transfer by neutral molecules. In the theory developed by Yu. I. Harkats [3] the expression for the total flux of ions is

$$q_i = n_i v - D_i \nabla n_i - \frac{D_i z_i E F}{RT} n_i - D z_i \nabla n_A. \tag{4}$$

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TABLE 1. The Degree of HCl Electrolytical Dissociation in Terms of Measured Electric Conductivity α_1 and E.m.f. α_2

C_{HCl}, mole/liter	0.003	0.08	0.3	3.0	6.0	16.0
α_1	0.986	0.957	0.903	—	—	—
α_2	0.99	0.88	0.773	1.402	3.4	13.2

The last term in (4) takes into account ion transfer by a flux of neutral molecules; here the concentrations of anions, cations, and neutral dissociated molecules are determined by the chemical equilibrium conditions

$$\beta = \frac{(n^-)^{z^+}(n^+)^{z^-}}{n_A}, \tag{5}$$

where β is the dissociation equilibrium constant. If the degree of dissociation at the prescribed total concentration n is α, then $n_A = (1-\alpha)n$ and, consequently,

$$\beta = \frac{\alpha^2 n}{1-\alpha}. \tag{6}$$

The dissociation constant β, unlike the degree of dissociation, must not depend on concentration. However, in real partially dissociated electrolytes those arguments for α and β are in rather poor agreement with experiment. In [11] the dissociation degree for HCl is listed in Table 1 as a function of concentrations, calculated in terms of measured electric conductivity α_1 and e.m.f. α_2.

Inspection of the table reveals that the dissociation degrees obtained by different experimental methods coincide best in the case of dilute solutions. In the high-concentration range of the electrolyte, α_2 even exceeds unity, which, naturally, has no physical sense.

According to the Arrhenius theory the dissociation constant β for the given electrolyte at the prescribed temperature and pressure must remain constant independently of the solution concentration. In [5], the dissociation constants of some electrolytes are given at their different concentrations. Only for very weak electrolytes (solutions of ammonia and acetic acid) does the dissociation constant remain more or less constant on dilution. For strong electrolytes (potassium chloride and magnesium sulfate), it changes by severalfold and in no way may be considered a constant.

Of course, one may formally take into account the dependence of the dissociation constant on the electrolyte concentration and use it in the modified Nernst-Planck equation (4), (5) but the main drawback in describing separately the diffusion and migration of ions in an electrolyte, in D. I. Mendeleev's opinion, lies in the fact that the interaction of particles of a dissolved substance between each other as well as with solvent molecules is neglected. Also, he has pointed out that not just the processes of formation of new compounds with solvent molecules are of importance for solutions. D. I. Mendeleev's viewpoints have been extended by A. I. Sakhanov [5], who believed that in addition to the usual dissociation reaction in an electrolyte solution there also proceeds associating of simple molecules. Molecular associations dissociate, in their turn, into complex and simple ions. In this case Eq. (4) will not hold mainly because of the fact that the expressions for diffusion, migration, and nondissociated flows of molecules must be determined relative to some mean liquid velocity. In concentrated solutions, this velocity does not coincide with the solvent velocity and must be determined from the fluid dynamics equations of a multicomponent mixture in which characteristics of its components (physical density, charge, diffusion coefficient of a complex ion) are, in fact, unknown. This is a reason why the theory of diffusion and migration of ions for a partially dissociated electrolyte solution, with a current traversing through it, encounters crucial difficulties. Besides, it is rather difficult to take an account of the force interaction of complex cations and anions between each other and with an external electric field. Therefore Einstein's formula (1) will also change its form.

The main drawbacks of the theory of electrolytic dissociation are fully defined in collected papers "Fundamental Principles of Chemistry" by D. I. Mendeleev as well as in [5, 6].

In our opinion, the principal disadvantage of the approaches considered above lies in the fact that the Nernst-Planck equation as well as its modified form for a partially dissociated electrolyte (4) are based on the hydrodynamic theory of diffusion. We shall substantiate below that it is more reasonable to use the equations of thermodynamics of irreversible processes.

Macroscopic Electroneutrality of a Volumetric Electrolyte Solution. A typical feature of an electrolyte is its macroscopic neutrality due to mutual compensation of the space charge of cations and anions

$$\frac{\partial n_e}{\partial \tau} + \operatorname{div}(n_e \mathbf{v}_e) = \frac{\partial n_i}{\partial \tau} + \operatorname{div}(n_i \mathbf{v}_i). \tag{7}$$

In order to preserve quasi-neutrality in sufficiently large volumes and for sufficiently long intervals of time, it is necessary for the concentrations of anions n_e and cations n_i to be equal, i.e.,

$$z_e n_e - z_i n_i = 0. \tag{8}$$

The Poisson equation is more exact, which for a medium with constant permittivity ε has the form

$$\nabla^2 \varphi = -\frac{1}{\varepsilon \varepsilon_0}(z_e n_e - z_i n_i). \tag{9}$$

The Gibbs Paradox and Distinguishability of Cations and Anions in the Macroscopic Description of an Electrolyte Solution. The Gibbs paradox implies that no matter how close in their properties two somehow differing gases are, when mixed, the entropy is increased by one and the same quantity 2KN ln 2, while no increase in entropy is observed in the case of two absolutely identical gases. Such a jump in the entropy behavior with a continuous transition from gases close in their properties but somehow differing to absolutely identical gases lies behind the Gibbs paradox.

S. D. Haitun [7] singles out the following stages in solving the Gibbs paradox: thermodynamic, classical, statistical, informative, and "operational."

The "operational" stage deals with the evolution of views about the dependence of the quantitative determination of entropy (in particular, entropy of mixing) on the observer and the capabilities of his experimental apparatus. Yu. S. Varshavskii and A. B. Sheinin [8, 9] were the first to derive an "operational" quantitative expression for the entropy of mixing which represents the dependence both on the properties of the gases to be mixed and on the measurement error of an "identifying" tool. As is noted in those works, a study of a system on a molecular level may be reduced to identification of all constituent particles in the system. A set of means, which could allow such study, is given the name [8, 9] "an identifying tool." If gases are identical, then the identifying tool is not capable of discerning the molecules, and the amount of information is equal to zero ($\Delta S = 0$). If the tool identifies molecules correctly, then the probability of a molecule belonging to one of the components is 1/2. If gases A and B are dissimilar but hardly discernible, i.e., similar to such extent that when the identifying tool is operating, there is a nonzero probability 3 of an error in which molecule A is identified as B and vice versa, then the uncertainty of this situation is determined by the Shennon informative entropy. The bulk of information I^* produced by the investigation of molecules is related to entropy as $\Delta S = KI^*N \ln 2$ [8, 9]; therefore

$$\Delta S = -2KN \ln 2\,[\omega \log_2 \omega + (1 - \omega)\log_2 (1 - \omega)]. \tag{10}$$

From (10) it is seen that the limiting cases $\Delta S = 0$ and $\Delta S = 2KN \ln 2$ are easy to obtain for $\omega = 0$ and $\omega = 1/2$ (well-discernible gases). Formula (10) ensures a continuous transition between those limiting cases, thus overcoming the difficulties which the Gibbs paradox involves.

When constructing the phenomenological theory of transfer processes in an electrochemical system, it is necessary to have the appropriate "*identifying tool*" to identify *real* flows of cations and anions. In practice, only *observable* flows (masses, charges, heat) are recorded; therefore it is conjectural even to pose the problem on discernibility of cations and anions in an electrolyte and treating them as independent components [10]. Nevertheless, when applying the Nernst-Planck equation (3) and its modified forms (4), it is implicitly postulated that cations and anions in the electrolyte solution are different components. The equations of transfer of cations and anions are written separately. On the other hand, the commonly used equation of electroneutrality (8) does not ensure, according to Gibbs [11], the independence of differentials of cations dn_i and anions dn_e; in a volumetric electrolyte solution their changes are functionally related and therefore they are identical, indiscernible components.

The Case of a Current Traversing a Binary Fully Dissociated Electrolyte. Let us write system of equations (3) in the form

$$\frac{\partial n_e}{\partial \tau} + \mathbf{v}\,\mathrm{grad}\, n_e = D_e \Delta n_e + \frac{z_e F D_e}{RT}\,\mathrm{div}\,(n_e \mathrm{E}), \tag{11}$$

$$\frac{\partial n_i}{\partial \tau} + \mathbf{v}\,\mathrm{grad}\, n_i = D_i \Delta n_i + \frac{z_i F D_i}{RT}\,\mathrm{div}\,(n_i \mathrm{E}), \tag{12}$$

$$z_e n_e - z_i n_i = 0. \tag{13}$$

Analogously to [11], instead of concentrations n_e and n_i we introduce the molar concentration related to n_e and n_i by the expressions

$$C = \frac{n_e}{z_i} = \frac{n_i}{z_e}. \tag{14}$$

Expressing n_e and n_i in Eqs. (11) and (12) in terms of the molar concentration, we arrive at the following expression for the function C:

$$\frac{\partial C}{\partial \tau} + \mathrm{v}\nabla C = D_{\mathrm{ef}} \Delta C, \tag{15}$$

where

$$D_{\mathrm{ef}} = \frac{D_e D_i (z_e + z_i)}{z_e D_e + z_i D_i} \tag{16}$$

is the diffusion coefficient of a salt or the effective diffusion coefficient of a binary electrolyte. Expressing the concentrations n_e and n_i in terms of the molar concentration C we find the expression for the vector of current density **J** [12]:

$$\mathbf{J} = (D_i - D_e) F z_i z_e \nabla C + \frac{F^2 z_i z_e}{RT} (z_i D_i + z_e D_e)\, C\mathrm{E}. \tag{17}$$

In [13] it is shown that by its meaning D_{ef} is a coefficient of molecular diffusion. For instance, the diffusion coefficients of copper sulfate have an intermediate value between the diffusion coefficients of copper and sulfate ions; if $D_e = 0.173 \cdot 10^{-9}\ m^2/sec$ and $D_i = 1.065 \cdot 10^{-9}\ m^2/sec$, then $D_{ef} = 0.854 \cdot 10^{-9}\ m^2/sec$. However, expression (16) does not offer an explanation of the abnormally high mobility of H and OH′ ions when their displacement proceeds by a croquet-like mechanism [14].

In system of equations (15)-(17) no symmetry of cross terms is observed; therefore it is difficult to take into account "the superposition effects." Indeed, from Eq. (17) it is evident that the molar concentration gradients ∇C exert an influence on the current J. On the other hand, one can see from Eq. (15) that an electric field has no effect on the diffusion of the molecules, and therefore the Onsager reciprocal relation is disturbed.

One may raise the objection that according to the Nernst-Planck equations it follows that the concentration gradients of cations and anions exert an influence on the potential distribution of an electric field [12]:

$$\nabla(\rho_R \nabla \varphi) = -F \sum_i z \nabla (D_i \nabla C_i). \tag{18}$$

However relation (18) itself has been derived by Neumann [13] on the assumption that the resultant current *does not depend on the mass flow.*

On derivation of the equations for diffusion and migration of ions in a volumetric electrolyte solution we shall employ the relations of the thermodynamics of irreversible processes.

Finally, it is worthy of note that in plasma physics there is also no symmetry of "the superposition effects" in describing the ambipolar diffusion of ions, and the theory is based on the hydrodynamic model [2].

In our opinion, electric field-induced transfer of charges entails transfer of their kinetic energy as well as of heat and mass, and conversely, mass or heat transfer may simultaneously cause, if we are concerned with the system of charged particles, charge transfer and give rise to an electromotive force.

The Equations of Electric Current-Induced Diffusion and Migration of Ions in a Volumetric Electrolyte Solution. For a macroscopic description of transfer processes in an electrolyte we shall use the equations of the thermodynamics of irreversible processes, which for conjugated flows and forces are of the form

$$\mathbf{q}_e = -L_{11}\nabla n - L_{12}\nabla\left(\frac{1}{T}\right) - L_{13}\nabla\varphi, \quad \mathbf{q}_0 = -L_{21}\nabla n - L_{22}\nabla\left(\frac{1}{T}\right) - L_{23}\nabla\varphi,$$
$$\mathbf{J} = -L_{31}\nabla n - L_{32}\nabla\left(\frac{1}{T}\right) - L_{33}\nabla\varphi, \tag{19}$$

where $L_{21} = L_{12}$, $L_{31} = L_{13}$, $L_{32} = L_{23}$. Let $D \equiv L_{11}$ be the molecular diffusion coefficient of an impurity; $\lambda \equiv L_{22}/T^2$ the thermal conductivity; $\rho_R \equiv L_{33}$ the electric conductance of an electrolyte; $D_A \equiv L_{13}$ the ambipolar diffusion coefficient; $D_T \equiv L_{12}$ the thermodiffusion coefficient.

The total flow of impurity with an account of convection may be written as

$$\mathbf{q}_s = n\mathbf{v}_l - D\nabla n - D_A\nabla\varphi. \tag{20}$$

where $\mathbf{q}_s$ is the salt flow; $\mathbf{v}_l$ is the liquid velocity.

The current with an account of the space charge is

$$\mathbf{J} = q\mathbf{v}_l - \rho_R\nabla\varphi + D_A\nabla n. \tag{21}$$

Then considering (21), the equations of nonstationary mass and charge transfer are (provided div $\mathbf{v}_l = 0$)

$$\frac{\partial n}{\partial\tau} + \mathbf{v}_l\,\nabla n = \operatorname{div}(D\nabla n) - \operatorname{div}(D_A\nabla\varphi), \tag{22}$$

$$\frac{\partial q}{\partial\tau} + \mathbf{v}_l\,\nabla q = \operatorname{div}(\rho_R\nabla\varphi) + \operatorname{div}(D_A\nabla n). \tag{23}$$

It is necessary to supplement Eqs. (22), (23) with the Poisson equation

$$\nabla^2(\varepsilon\varepsilon_0\varphi) = -q. \tag{24}$$

The dielectric permittivity of the solution may be substantially changed near electrodes or membranes. In this case a space charge emerges and a double electric layer is formed. In a volumetric solution, the electroneutrality condition is, as a rule, fulfilled with a high accuracy; therefore it will be assumed hereafter that condition (8) is fulfilled and, consequently, div($\mathbf{J}$) = 0. In this case Eqs. (22) and (23) are simplified to acquire the form

$$\frac{\partial n}{\partial\tau} + \mathbf{v}_l\,\nabla n = (D\nabla n) \pm \operatorname{div}(D_A\nabla\varphi), \tag{25}$$

$$\mathbf{J} = \rho_R(n)\,\nabla\varphi \pm D_A\nabla n \tag{26}$$

or

$$\operatorname{div}(\rho_R\nabla\varphi) \pm \operatorname{div}(D_A\nabla n) = 0. \tag{27}$$

For Eqs. (25) and (26) the corresponding boundary conditions are to be set. Their choice will be based on the Faraday laws. In the one-dimensional form they are as follows:

initial conditions:

$$\tau = 0, \quad n(x,\ 0) = n_0, \quad E(x,\ 0) = E, \tag{28}$$

boundary conditions:

$$x = 0 \quad q_s|_{x=c} = Jn_A, \tag{29}$$

$$x = 1 \quad q_s|_{x=1} = Jn_k, \tag{30}$$

where n_A, n_k are the electrochemical equivalents of the products of electrolysis liberated at the anode and the cathode. In order to take into consideration the parallel and secondary reactions, the notion of current efficiency has been introduced, which must be accounted for in conditions (29), (30).

In some cases the prescribed current $J(\tau)$ is passed through an electrolytic cell. In that case for time $\Delta\tau$ a new value of n and conductance $\rho_R(n)$ is determined, while from the equation

$$E = \frac{J}{\rho_R} - \frac{D_A}{\rho_R} \nabla n \tag{31}$$

the electric intensity across the cell is determined. Often the potential difference applied between electrodes in an electrochemical cell is preset. Then after calculating new concentration values for some moment of time, new values of current must be determined, which is constant in an electrochemical cell.

To determine transfer characteristics, i.e., D (molecular diffusion coefficient), D_A (ambipolar diffusion coefficient), ρ_R (conductance), it is necessary to use the methods of solving inverse problems and to have the necessary experimental information on the observed parameters $q(r, \tau)$, $n(r, \tau)$, $E(r, \tau)$.

In the case of diffusion in concentrated mixtures, mechanical equilibrium may be disturbed, and the mixture is transferred as a whole; therefore it is necessary to use the Navier-Stokes equation, namely,

$$\rho \left[\frac{\partial \mathbf{v}}{\partial \tau} + (\mathbf{v}\nabla)\mathbf{v} \right] = -\nabla P + \eta \left[\Delta \mathbf{v} + \frac{1}{3} \nabla (\operatorname{div} \mathbf{v}) \right]. \tag{32}$$

In system of Nernst-Planck equations (3), (4) n_i indicates the molar concentration of an electrolyte but as has been mentioned above, in real solutions not molecules but their associates dissociate, whose characteristics are, as a rule, unknown.

L. D. Landau was the first to describe diffusional-electrical phenomena in terms of the thermodynamics of irreversible processes without considering molecular diffusion of cations and anions as well as limitations on the electrolyte concentration [15].

Numerical Simulation of an Electric Current Passing through a Partially Dissociated Electrolyte with an Account of Concentration Polarization. Of interest is the influence of cross terms on diffusion and migration of ions in an electrolyte with a current passing through it. We consider a partially dissociated HCl solution in water. A constant current is passed through the electrolyte.

With an account of the results obtained earlier in the one-dimensional statement, we have the following system of equations:

$$\frac{\partial n}{\partial \tau} = \frac{\partial}{\partial x} \left(D \frac{\partial n}{\partial x} \right) - \frac{\partial}{\partial x} (D_A E), \tag{33}$$

$$J = \rho_R E + D_A \frac{\partial n}{\partial x}. \tag{34}$$

Boundary conditions are as follows:

$$\tau = 0 \quad n(x,\ 0) = n_0, \quad J = \text{const}, \tag{35}$$

$$x = 0 \quad q_s|_{x=0} = Jn_A, \tag{36}$$

$$x = 1 \quad q_s|_{x=1} = Jn_k. \tag{37}$$

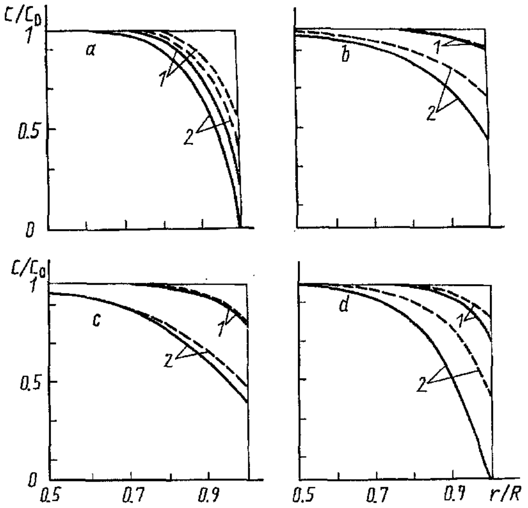

Fig. 1. Concentration field on passing a constant current through the electrolyte: a) C = 30 kg/m^3, J = 50 A/m^2: 1) T = 0.29 · 10^5 sec, 2) 0.38 · 10^5; b) C = 50 kg/m^3, J = 500 A/m^2: 1) T = 0.5 · 10^4 sec, 2) 0.45 · 10^5; c) C = 20 kg/m^3, J = 5 A/m^2: 1) T = 0.4 · 10^5 sec, 2) 0.198 · 10^6; d) C = 50 kg/m^3, J = 50 A/m^2: 1) T = 0.1875 · 10^5 sec, 2) 0.69 · 10^5. Solid lines: $D_A = 0.1 \cdot 10^9$ A/(m·kg); dashed lines: $D_A = 0$.

According to [14] we may write the diffusion coefficient of HCl as

$$D_{HCl} = \left(3{,}07 + \frac{1}{2} n_m\right) \cdot 10^{-9} \ \mathrm{m^2/sec} \tag{38}$$

The dependence of conductance on electrolyte concentration is as follows according to [14]:

$$\rho_R = (40 + 7n_m) \cdot 10^4 \ 1/(\Omega \cdot \mathrm{m}). \tag{39}$$

We emphasize once more that using the Nernst-Planck equation and the electroneutrality, one fails to obtain an additional term in Eq. (33).

To elucidate the influence of ambipolar diffusion, calculations have been made in two variants: $D_A = 0$ (dashed lines in Fig. 1) and $D_A = 0.1 \cdot 10^{-9}$ A/(m·kg) (solid lines). Inspection of the figure reveals that at current densities higher than 5 A/m^2, the contribution of the ambipolar diffusion is significant. The coefficient D_A should be determined experimentally since its theoretical values point only to an order of magnitude.

Conclusion. To phenomenologically describe diffusional-electrical phenomena in electrolytes it is suggested to use the methods of the thermodynamics of irreversible processes, rather than the hydrodynamic theory of diffusion of ions, for the experimentally observable thermodynamic flows and forces without clear discernment and identification of *real* ion flows and mobilities.

NOTATION

D, molecular diffusion coefficient, m^2/sec; D_i, diffusion coefficients of anions and cations, m^2/sec; D_A, ambipolar diffusion coefficient, A/(m·kg); F, Faraday's constant, 96.985 C/eq.; J, current density, A/m^2; R, universal gas constant; n, concentration, kg/m^3; n_A, concentration of neutral molecules, kg/m^3; n_i, concentration of dissociated molecules, kg/m^3; n_m, molar concentration, g·eq./liter; E, electric field intensity β, equilibrium constant; α, degree of dissociation; ε, dielectric constant; k, Boltzmann constant; ρ_R, conductance.

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