DIFFUSIONAL-ELECTRICAL PHENOMENA IN ELECTROLYTES

N. N. Grinchik

UDC 539.217.1+541.135+531.391.2:536.24

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 $z_i eE$, 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:

$$u = \gamma_i^* z_i eE,$$

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

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

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:

$$q_i = n_i v - D_i \nabla n_i + \frac{D_i z_i eE}{RT} n_i.$$

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

$$q_i = n_i v - D_i \nabla n_i - \frac{D_i z_i eE}{RT} n_i - D z_i \nabla n_A.$$
TABLE 1. The Degree of HCl Electrolytical Dissociation in Terms of Measured Electric Conductivity $\alpha_1$ and E.m.f. $\alpha_2$

<table>
<thead>
<tr>
<th>$C_{\text{HCl}}$ mole/liter</th>
<th>0.003</th>
<th>0.08</th>
<th>0.3</th>
<th>3.0</th>
<th>6.0</th>
<th>16.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_1$</td>
<td>0.986</td>
<td>0.957</td>
<td>0.903</td>
<td>$-$</td>
<td>$-$</td>
<td>$-$</td>
</tr>
<tr>
<td>$\alpha_2$</td>
<td>0.99</td>
<td>0.88</td>
<td>0.773</td>
<td>1.402</td>
<td>3.4</td>
<td>13.2</td>
</tr>
</tbody>
</table>

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

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

(5)

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

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

(6)

The dissociation constant $\beta$, unlike the degree of dissociation, must not depend on concentration. However, in real partially dissociated electrolytes those arguments for $\alpha$ and $\beta$ 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 $\alpha_1$ and e.m.f. $\alpha_2$.

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, $\alpha_2$ even exceeds unity, which, naturally, has no physical sense.

According to the Arrhenius theory the dissociation constant $\beta$ 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