Transport in dilute solutions

1 Introduction

For a dilute solution of i electrolytes in an un-ionised solvent at constant temperature and pressure, one can write down six equations describing transport of mass and charge [1].

1.1 The flux of a dissolved species

The flux of each dissolved species i - defined as the number of ions moving in a certain direction per unit of surface and time ($mole/m^2s$) - is due to **convection**, **diffusion** and **migration**.

Convection is caused by the movement of a particle together with the whole fluid. In case of dilute solutions, one considers the fluid's motion to be unaffected by the ions. Therefore the flux due to convection is only determined by the velocity of the fluid $\overline{v}$ and the concentration c_i of the ion.

Diffusion takes place when the concentration on an ion differs from point to point in a solution. The ions will move until one becomes an uniform distribution of all ions in the solvent. This movement is well described by Fick's law, which says that the diffusion is proportional and opposite to the gradient of the concentration. This proportionality is described by the factor D_i which can be considered to be constant.

Charged particles can also move due to external electrical forces. In this case, one speaks of **migration.** A charged particle in an electrical field will experience a force proportional to his charge ($\overline{F} = q\overline{E}$). When a force acts upon a particle, it accelerates causing the friction force to limit the velocity. The flux due to migration is function of the charge, the concentration and the electrical field. This proportionality is given by the mechanical mobility u_i.

The total flux $\overline{N}_i$ of an ion i due to convection, migration and diffusion is therefore given by

$$\overline{N}_i = -z_i u_i F c_i \overline{\nabla} U - D_i \overline{\nabla} c_i + c_i \overline{v} \tag{1.1}$$

with:

c_i: the concentration in $mole/m^3$,

$\overline{v}$: the velocity of the solvent in m/s,

z_i: the charge number,

u_i: the mechanical mobility in $m^2 mole/Js$,

$\overline{\nabla} U$: the gradient of the potential ($\overline{E} = -\overline{\nabla} U$) in V / m,

D_i: the diffusion coefficient in m^2/s,

$\overline{\nabla} c_i$: the gradient of the concentration field in $mole/m^4$,

F: the constant of Faraday in C / mole.

Remarks:

- When the solution is less dilute, one can use the gradient of the electrochemical potential $\tilde{\mu}_i$ as the driving force for diffusion and migration [1].
- To become this equation one neglected the interactions of species with other solutes.
- In semiconductor materials one can write exactly the same equation for the flux of the electrons, holes, donors and acceptors but with the solvent velocity equal to zero.

1.2 The current density

An electric current is a consequence of the movement of charged particles, ions in our case. Since one has an expression for the flux of each charged particle, the current density is easily obtained by adding each flux multiplied by the corresponding charge per mole:

$$\bar{J} = F\sum_i z_i \bar{N}_i \tag{1.2}$$

1.3 Conservation of mass

For each species i one can state that at each point of the solution, the change of concentration is equal to the net input plus the local production due to chemical reactions:

$$\frac{\partial c_i}{\partial t} = -\bar{\nabla}.\bar{N}_i + R_i \tag{1.3}$$

with:

$\bar{\nabla}.\bar{N}_i$: the divergence of the flux vector,

R_i : the production rate of an ion (pos. of neg.) due to homogeneous reactions in the bulk of the solution. Reactions often are restricted to electrode surfaces, in which case R_i equals zero.

1.4 The Poisson equation or electroneutrality

The charge density at each point of the solution is the algebraic sum of the charges of all dissolved particles and is given by the Poisson equation:

$$F\sum_i z_i c_i = -\varepsilon \bar{\nabla}^2 U \tag{1.4}$$

with ε the dielectric constant of the solution.

When the charge is zero at each point then the solution is said to be electro-neutral. For an electrolyte, the conductivity is so large that free charges do not exist. Hence one can replace the Poisson equation by the one expressing the electroneutrality:

$$\sum_i z_i c_i = 0. \tag{1.5}$$